

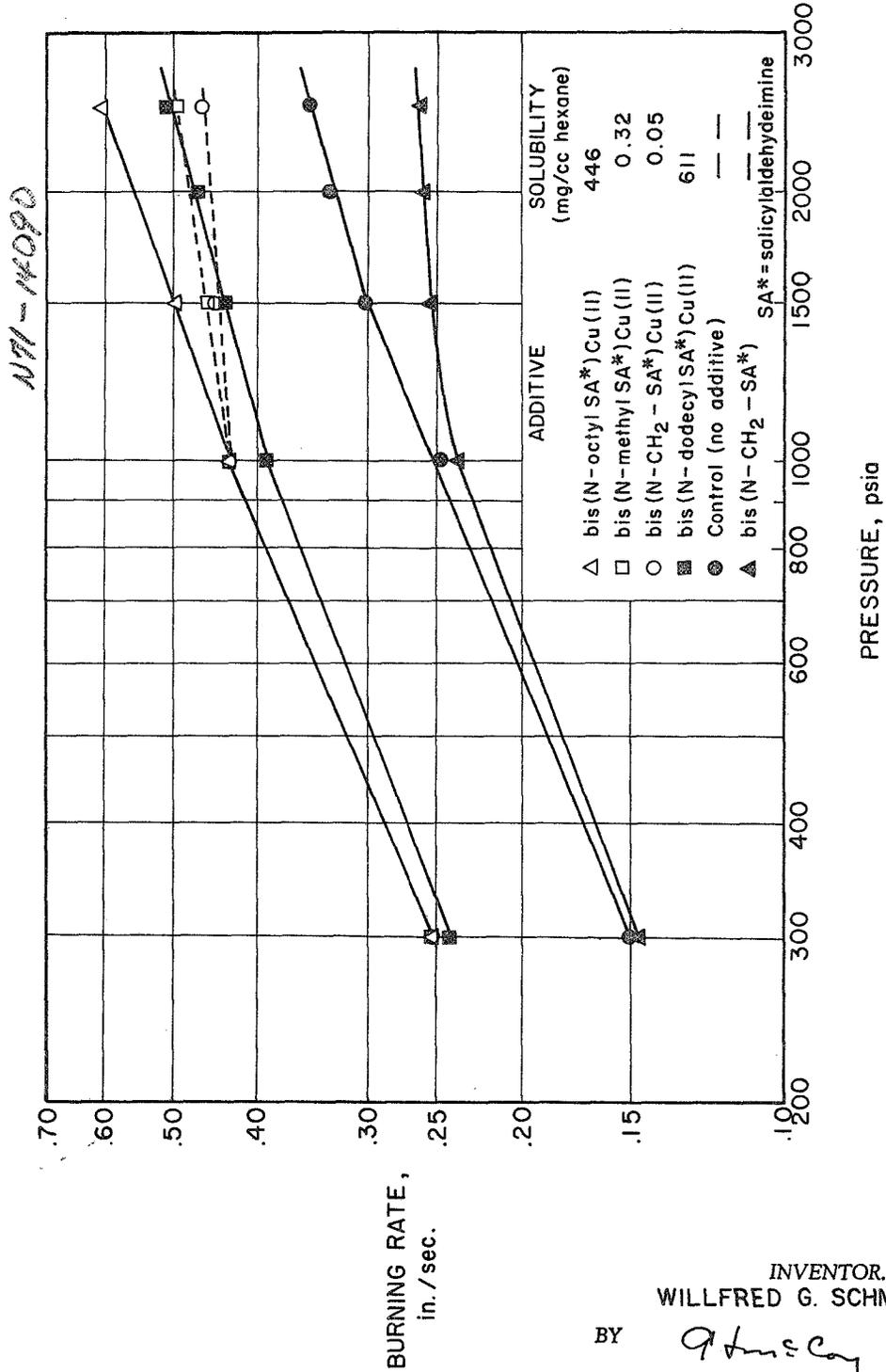
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DEPUTY ADMINISTRATOR OF THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
AMMONIUM PERCHLORATE COMPOSITE PROPELLANT CONTAINING AN ORGANIC TRANSITIONAL METAL CHELATE CATALYTIC ADDITIVE  
Filed Sept. 11, 1968



BURNING RATE,  
in./sec.

PRESSURE, psia

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*348*

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3,492,176

**AMMONIUM PERCHLORATE COMPOSITE PROPELLANT CONTAINING AN ORGANIC TRANSITIONAL METAL CHELATE CATALYTIC ADDITIVE**

T. O. Paine, Deputy Administrator of the National Aeronautics and Space Administration, with respect to an invention of Willfred G. Schmidt, Sacramento, Calif.

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2 Claims

**ABSTRACT OF THE DISCLOSURE**

A catalytic additive for ammonium perchlorate composite propellants, resulting in an acceleration of the burning rate of said composite propellants with approximately a normal pressure slope up to 1000–1200 p.s.i., but with a small pressure exponent at higher pressures, comprised of transition metal chelates whose ligands have at least one basic nitrogen.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of section 305 of the National Aeronautics and Space Act of 1958, Public Law 85–568 (72 Stat. 435; 42 U.S.C. 2457).

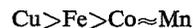
This invention relates primarily to the development of an improved catalyst for use with an ammonium perchlorate oxidized composite fuel mixture. Previously, catalysts for this type of fuel mixture included inorganic salts and oxides of transition metals. These prior art catalysts, although they effectively accelerated the burning rate of the propellant, did not lower the pressure slope at high pressures and this often resulted in uneven deflagration and sometimes detonation. In order to mitigate this occurrence, a number of complex compounds had to be added to the composite fuel mixture. The present invention is an attempt to achieve all of the advantageous features of the prior art catalysts while minimizing the disadvantages thereof.

It is therefore an object of the present invention to provide a single, readily synthesized compound that may be easily added to an ammonium perchlorate composite fuel mixture and which yields an acceleration of the burning rate of the mixture while at the same time having a low pressure exponent at the high pressures of 1200–3000 p.s.i.

The drawing illustrates the various slopes of burning rate vs. pressure for some copper II N-substituted salicylaldehydeimines. The present invention developed out of an investigation of reactions and mechanisms which occur in the substrate at or below the burning surface of perchlorate containing propellants in order to determine their contribution to the overall processes which are involved in the deflagration and combustion of solid propellants. Ambient pressure differential thermal analyses were performed on ammonium perchlorate composite fuel mixture containing various types and amounts of catalytic materials. Variables such as particle size and fuel were kept constant. Pressure, however, was a variable the effect of which was investigated. Catalysts studied included various inorganic oxidizers and organic chelating agents. Such organic chelating agents as the ethanalamine series, i.e., mono, di, and tri ethanalamine salicylaldehydeimine, acetylacetonate, phthalocyanine, and 8-hydroxyquinoline were coordinated with transition metals such as copper, manganese, iron, and cobalt. It was found that most effective catalysts are those transition metals having two stable oxidation states which involve a one-electron change. In

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this respect, it was found that the catalytic effectiveness order of the metals hereinbefore mentioned is



5 at pressures below 1000 p.s.i. This resulted because the two most stable states of manganese (+2 and +4) are separated by two electrons, while the +3 state of cobalt is unstable (due to the potential, -1.8 v., of this couple). At higher pressures, this order breaks down. Copper has been found, however, to be the most effective over the entire range.

10 Most metallic additives affect the high temperature decomposition of ammonium perchlorate. In the uncatalyzed case, this decomposition does not become appreciable until approximately 400° C. However, in the presence of catalysts, rapid decomposition rates may occur as low as 260° C. (just above the ammonium perchlorate transition). As hereinbefore stated, most of the previous catalysis has been done with transition metal oxides. The approach of the present invention is to use transition metal chelates as additives. In this way, variation in bonding of the metal and control of the conditions affecting combustion of the propellant are more efficiently effectuated. One of the most versatile series of chelates are the salicylaldehydeimine Schiff bases. The coordinated bonding of these compounds is through the oxygen and nitrogen atoms of the ligand. Other useful chelates are those in which at least one of the bonding atoms is a part of the ring structure. These latter are more stable thermally although the thermal stability of the salicylaldehydeimine can be increased when the two ligands are connected with a bridge such as ethylene diimine. It has been found that linking an alkyl chain to the nitrogen results in increased solubility in the fuel. However, experimental results indicate that the more insoluble materials result in a leveling off of the pressure slope (of a burning rate vs. pressure graph) at pressures above 1000 p.s.i. The drawing, which is a plot of the burning rate of salicylaldehydeimine-copper II chelates having various N-substituted groups versus pressure, shows that the pressure slope above 1000 p.s.i. is much lower for the insoluble additives [i.e., bis (N-methyl salicylaldehydeimine) Cu (II) and bis (N-CH<sub>2</sub>-salicylaldehydeimine) Cu (II)] than it is for the more soluble ones [i.e., bis (N-octyl salicylaldehydeimine) Cu (II) and bis (N-dodecyl salicylaldehydeimine) Cu (II)]. It also shows that in general the chelates are very effective catalysts over the entire range of pressure.

25 Prior studies indicate that the exothermic decomposition of ammonium perchlorate most probably influences the combustion rate of ammonium perchlorate fuel composite propellants. Experimental results indicate that the decomposition of ammonium perchlorate under high heat fluxes and the catalytic decomposition under moderate heat fluxes involves the decomposition of perchloric acid formed by the dissociation of the ammonium perchlorate. It was found that the decomposition of ammonium perchlorate having heterogeneously added catalysts proceeded the same way under ammonia and nitrogen atmospheres, as it normally does. Since under NH<sub>3</sub> the equilibrium lies almost entirely on the side of the undissociated material, the catalysis appears to be in the solid phase. The perchloric acid decomposition could be similar in solid phase even if the proton is not fully transferred. At temperatures where both NH<sub>4</sub><sup>+</sup> and ClO<sub>4</sub><sup>-</sup> are freely rotating it would be possible to have an intermediate NH<sub>3</sub> . . . H . . . OClO<sub>3</sub>, whose catalyzed decomposition would be similar to HClO<sub>4</sub>. The products of this decomposition can then further react with NH<sub>4</sub><sup>+</sup> (or NH<sub>3</sub>). Studies have indicated that the initial step in the catalysis may be a reaction between the metal chelate and the ammonium ion which is then followed by an interaction of

one of these products and the perchlorate ion. This second step results in the exothermic part of the reaction.

A generalization can therefore be made that for a given amount of metal there is a greater effect if the metal is bound in some organo-metallic compound (or chelate) than if it is present as an ionic salt or oxide. The catalyst affects the proton transfer equilibrium by removing one of the products thereby driving the reaction forward. It does this by affecting the heterogeneous decomposition of perchlorate acid. There are several reasons why an organo-metallic compound would be expected to be more effective than an oxide in this reaction: (1) if the organo-metallic first decomposes to the oxide it would be in molecular size particles with fresh surfaces, i.e., formed in situ, and (2) if the catalyst is the original additive or a metal-organic product of an earlier interaction, a similar result would be expected as not only do metals promote  $\text{HClO}_4$  decomposition,  $\text{HClO}_4$  reacts exothermically with most organic substances. With an organo-metallic additive, both processes could occur, with the possibility of an overall additive effect on the rate of decomposition of the  $\text{HClO}_4$ .

Further evidence for the decomposition of  $\text{HClO}_4$  being one turn in the overall kinetics of combustion of an ammonium perchlorate composite propellant comes from the stabilizing effect derived from small amounts of an added base. When propellants were formulated with 1 percent tertiary amine (tributyl and dimethyl dodecyl), the resultant propellant had a greatly reduced burning rate and pressure exponent. Since there is only 1 percent of the basic amine for 75 percent of ammonium perchlorate, the effect is most likely a surface effect, possibly the neutralization of  $\text{HClO}_4$ . This would still allow  $\text{NH}_3$  to desorb while both slowing the desorption of  $\text{HClO}_4$  and stabilizing the  $\text{HClO}_4$  at the crystal surface by forming a more stable salt with it. The difference in slope between the soluble and insoluble copper chelates (as in the drawing) with the basic salicylaldehydeimine ligand may be

explained due to the difference in availability of the base at the oxidizer surface. The basic portion of the soluble chelate was not as available (tied up in the binder) as that from the insoluble chelates and therefore had less or no effect on the burning rate.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. The combination of an ammonium perchlorate composite propellant and an organic transitional metal chelate catalytic additive for said propellant, the improvement comprising:

said additive being selected from organic chelating agents in the group consisting of the mono, di, and tri ethanalamines series, salicylaldehydeimine, acetylacetonate, phthalocyanine and 8-hydroxyquinoline, said selected organic chelating agent being coordinated with a transition metal selected from the group consisting of copper, manganese, iron and cobalt.

2. The combination of claim 1 wherein:

said additive is a readily synthesized transition metal chelate selected from the group consisting of  
 (a) bis(N-octyl salicylaldehydeimine) Cu II,  
 (b) bis(N-methyl salicylaldehydeimine) Cu II,  
 (c) bis(N- $\text{CH}_2$ -salicylaldehydeimine) Cu II, and  
 (d) bis(N-dodecyl salicylaldehydeimine) Cu II.

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