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PRODUCTION OF AMMONIUM NITRATE-FUEL OIL BLASTING AGENTS WHICH WHEN DETONATED RESULT IN GASEOUS MIXTURES OF LOW TOXICITY

Henryk S. Berczely, Orrantía del Mar, Lima, Peru, assignor to Explosivos S.A., Pisco, Lima, Peru, a corporation of Peru

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This invention relates to the production of mixtures of ammonium nitrate and fuel oil which when detonated result in gaseous mixtures which are of low toxicity, and non-toxic to humans, and more particularly to the process of producing such mixtures involving a simple and readily applicable control to insure proper proportionment of the ammonium nitrate and the fuel oil, so that, when the resultant mixture is detonated, the gaseous products produced are of low toxicity and not toxic to humans.

Mixtures of 94.0% to 94.5% of ammonium nitrate and 5.5% to 6% suitable petroleum oils, usually No. (Class) 2 diesel fuel oil, called Akremite or ANFO, have been recommended recently for underground blasting, using conventional dynamites for the detonation of the mixture.

One of the basic conditions for the use of explosives in underground blasting operations is that the fumes of the explosions should have a minimum quantity of toxic gases and should not be toxic to humans, thus avoiding fatal accidents. Conventional explosives made with a nitroglycerine base are closely controlled by the manufacturers to obtain this result. The investigations of the "U.S. Bureau of Mines," published in the Symposium of the Missouri School of Mines and Metallurgy in 1959, have shown that the toxicity of the fumes resulting from the explosion of the ANFO mixture depends on the relative proportions of the ammonium nitrate and fuel oil. According to these investigations the quantity and composition of the fumes or gaseous atmosphere produced by the explosion is not markedly different from the quantity and composition of the fumes produced in the explosion of the commercial dynamites, when the content of the fuel oil in the ANFO is strictly maintained between 5.5% and 6%, the detonation properly made and there is no excessive humidity in the mixture. Reducing the percentage of fuel oil in the mixture below 5.5% results in a high quantity of extremely toxic nitrogen dioxide (NO_2 or N_2O_4) in the fumes of the explosion.

According to Bulletin 272 of 1941 of the United States Public Health Service, nitrogen dioxide is about 40 times more toxic than carbon monoxide. Since the density of nitrogen dioxide is higher than that of air, a longer time is required to dissipate nitrogen dioxide by diffusion than is required for carbon monoxide, whose density is equal to air.

The Conference of the Governmental Industrial Hygienists of the United States established in 1954 that the maximum amount of allowable concentration of nitrogen dioxide for an 8-hour exposure is 5 parts nitrogen dioxide per million parts of air. Higher concentrations in the air may cause severe lung irritations, the symptoms of which are delayed for several hours, even for several days. In comparison, carbon monoxide can be tolerated for an 8-hour exposure in a concentration of 100 parts of CO per million parts. It is also known that a concentration greater than 200 parts of nitrogen dioxide per million causes incurable illness, and that 0.025% (250 p.p.m.) in the air is the lethal limit. According to Bulletin 272 of the United States Public Health Service, until 1941, accidents in the industry caused 107 deaths due

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to nitrogen dioxide, a statistic which does not include the number of non-fatal accidents.

My investigation has shown that ammonium nitrate fuel oil mixtures containing 3.5% fuel oil, when detonated, produces fumes having a content of nitrogen dioxide approximately 15 times greater than the fumes of conventional explosives, such as nitroglycerine base explosives. Moreover, the concentration of nitrogen dioxide exceeds the lethal limit of 0.025%. Using fuel oil in amount greater than 6% reduces the sensitivity of the ammonium nitrate fuel oil mixture to detonation. Such mixtures containing 7.5% fuel oil gave 4 misfires or failures in nine applications.

In this specification all percentages are on a weight basis unless otherwise indicated or apparent.

Visual comparison of ammonium nitrate fuel oil mixtures containing 3.5%, 5.7% and 7.5% of fuel oil does not reveal the difference in fuel oil concentration. Such mixtures look alike; the differences therebetween are almost imperceptible especially when ammonium nitrate prills with high absorption power for fuel oil are used. Accordingly, the appearance of the mixture does not reveal whether the mixture has been properly proportioned, or whether an error has been made in the fuel oil content. Such error in the proportionment of the mixture can readily occur when weighing out the ammonium nitrate or the fuel oil or due to inadequate functioning of the mixers or of the feeders of these materials to continuous mixers with consequent change in the composition of the mixture producing mixtures with less or more of fuel oil than the desired range of from 5.5% to 6%.

The report of investigations 6015 of the U.S. Bureau of Mines referring to the fire and explosion in the ANFO-mixing building in Norton, Virginia, that occurred on December 27, 1961, shows that in this mixing plant there did not exist any process or apparatus to check the uniformity of the mixing or the content of the fuel oil in the ANFO. This report is of particular interest because other plants are operated under identical conditions. The mixing of ammonium nitrate fuel oil in itself is already a dangerous operation, if executed without usual precautions observed by the explosive manufacturers, but the lack of control of the uniformity of the ANFO, or of its fuel oil content, is still more dangerous, because the fumes produced by the detonation of ANFO with low fuel oil content may affect the life and the health of an unlimited number of miners in underground blasting operations.

It is a principal object of the present invention to provide a method of controlling the proportionment of ammonium nitrate and fuel oil to insure mixture thereof in such proportions that when detonated the gaseous products produced are of low toxicity, i.e., contain appreciably less than the amount of nitrogen dioxide toxic to humans.

It is another object of this invention to provide a process for controlling the mixing of ammonium nitrate with fuel oil which renders it immediately apparent when any error has occurred in the amount of fuel oil used and without requiring the use of complicated physical or chemical analysis to determine the fuel oil content or the relative proportions of the constituents of the mix.

Other objects and advantages of this invention will be apparent from the following detailed description thereof.

In accordance with this invention a new, safe and simple procedure is provided involving coloring the ammonium nitrate with a dyestuff dissolved in the fuel oil. Any dyestuff which can be readily dissolved in the fuel oil, which dyestuff is chemically inert with respect to the ammonium nitrate and which imparts a distinctive color to the ammonium nitrate fuel oil mixture such as to enable ready

differentiation between the colored ammonium nitrate fuel oil mixture and such admixture made with uncolored fuel oil, can be used. The amount of dyestuff thus employed is the amount required to impart a distinctive color to the mix and hence will vary with different dyestuffs. In general the use of about 0.05% to 0.5% dyestuff based on the weight of fuel oil will be found adequate. It is important that the dyestuff used be soluble in the fuel oil; unless the dyestuff is dissolved in the fuel oil, and thus each particle of fuel oil is dyed to the same extent, so that the relative distribution of the dyed fuel oil throughout the ammonium nitrate is readily apparent upon visual inspection, the advantages hereinafter pointed out are not obtained.

In accordance with one aspect of this invention, the admixture of the ammonium nitrate with the fuel oil containing the dissolved dyestuff enables ready and prompt ascertainment of whether or not the fuel oil is substantially homogeneously dispersed throughout the ammonium nitrate. Should the fuel oil be concentrated in greater amounts in certain portions of the ammonium nitrate than others, this will be readily apparent from the difference in color of those portions containing different amounts of the colored fuel oil. By having the fuel oil uniformly and homogeneously distributed throughout the ammonium nitrate, the resultant mixture when detonated will not contain in any portions thereof relatively small amounts of fuel oil below about 5.5%, which small amounts cause the formation of fumes containing dangerous or highly toxic amounts of nitrogen dioxide.

In accordance with another aspect of this invention, for any given dyestuff employed with the fuel oil a small reference sample is prepared containing the dyed fuel oil and the ammonium nitrate in the proper portions, namely, from 94.0% to 94.5% ammonium nitrate and 5.5% to 6% fuel oil. This reference sample is used as the standard or comparison sample. By comparing the color of the mixture produced by batch or continuous mixing of ammonium nitrate and the dyed fuel oil with the color of the reference sample containing of course the same dyestuff in the same relative amounts, one can tell immediately whether or not the proportions of the ammonium nitrate and fuel oil are correct.

Moreover, the present invention discloses readily whether the distribution of the fuel oil and the ammonium nitrate is uniform, i.e., whether the fuel oil is uniformly distributed throughout the ammonium nitrate. A uniformly colored mix insures the presence of a uniform mixture. On the other hand, a heterogeneous mixture in which the fuel oil is not uniformly distributed throughout the ammonium nitrate is immediately apparent by the splotchy or different colored appearance.

The following examples are given for illustrative purposes. It will be understood the invention is not limited to these examples.

In the examples readily available, commercial dyestuffs were used—the Yellow Sudan 3G, Color Index 2822, reference No. 12700; the Black Sudan BB, Color Index 2899, reference No. 26,150. The Grease Red BB, reference No. 26,125, as well as the other two dyestuffs are commercially available oil-soluble organic dyestuffs chosen for exemplary purposes. As indicated, other dyestuffs soluble in the fuel oil and which impart characteristic color thereto chemically inert to the ammonium nitrate can be used.

EXAMPLE I

11.4 kg. of fuel oil #2 colored with 4.7 grams of Yellow Sudan 3G per liter dissolved in the fuel oil were mixed with 188.6 kg. of ammonium nitrate in prills of 2–4 mm., coated with an organic anticaking product. The mixer used was a kneader with two horizontal blades, rotating in opposite directions and the mixing was stopped when the prills had reached a uniform coloration.

A sample of this colored mix of ammonium nitrate and

fuel oil was used as a reference sample and additional mixes prepared employing the reference sample as the standard, which different mixes were in every case compared with the standard to obtain substantially the same color. Chemical analysis of the different mixes thus prepared showed that the fuel oil content varied from 5.64% to 5.83%. The concentration of fuel oil in the reference sample and that considered the theoretical optimum is 5.7%. This demonstrates the efficiency of the process to obtain proper proportionment of the ammonium nitrate and the fuel oil.

EXAMPLE II

188 kg. of ammonium nitrate, fertilizer grade, were mixed with 12 kg. of fuel oil #2, colored with 0.5 gram of Black Sudan BB per liter dissolved in the fuel oil, in a double motion paddle mixer. When the coloration appeared uniform, the mixing process was stopped.

Samples of the uniformly colored mixture were taken and analyzed to determine their fuel oil content. Analysis showed a variation of from 5.87% to 6.16%, demonstrating that the uniformity of the color of the mixture employing the dyed fuel oil is an accurate indication of the homogeneous character of the mixture.

Comparative Example III

A mixture of ammonium nitrate with fuel oil containing 5.7% fuel oil colored with Grease Red BB dissolved in the fuel oil in amount of 0.7 gram of this dyestuff per liter was produced following the procedure of Example I.

For comparative purposes a second mixture was produced by mixing 192 kg. of crystalline ammonium nitrate with 8 kg. of fuel oil colored with 0.7 gram of Grease Red 5B per liter using the same procedure. This comparative mixture contained only 4% fuel oil. Visual inspection of both mixtures showed immediately the lack of fuel oil in the comparative mixture.

Comparative Example IV

184 kg. of ammonium nitrate of equal quality as that used in Example I were mixed with 16 kg. of fuel oil colored with 4.7 grams of Yellow Sudan 3G per liter dissolved in the fuel oil, in a mixer described in Example II. Comparing the coloration intensity of the mixture, which intentionally contained 8% fuel oil, to a control mixture with a 5.7% fuel oil content, colored with the same dyestuff, the excess of fuel oil was immediately noticed. Observing the two mixtures through a monochromatic filter of 4,700 Angstrom, the difference was even more pronounced.

EXAMPLE V

Into a mixer provided with a horizontal blade stirrer is introduced from one side, the ammonium nitrate and fuel oil dyestuff solutions containing 0.7 gram Grease Red BB per liter, by means of feeders which maintain the weight ratio of 94% ammonium nitrate to 6% colored fuel oil. The horizontal blade stirrer mixes the two ingredients and at the same time pushes them from the entrance side to the other side of the mixer, where the finished mixture is discharged by an endless screw, to be packed. A conventional colorimeter is employed at the discharge side of the mixer sensitive to the color of the mixture. This colorimeter is adjusted for a predetermined color of the mix determined by the dyestuff used and the resultant color of the mixture containing proper proportions of about 94.0% to 94.5% ammonium nitrate and 5.5% to 6% fuel oil. Any appreciable deviation from this color causes the colorimeter to energize an alarm signal, so that the operator can stop the mixing process and make the necessary adjustment to produce a mix having the proper proportions.

The above examples are exemplary only and the invention is not confined thereto but includes modifications such as the use of dyestuffs other than those mentioned, and use of dyestuffs in different concentrations to pro-

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duce colored fuel oils in which the dyestuff is dissolved in the fuel oil. The ammonium nitrate fuel oil mix can contain, in addition to the dyestuff dissolved in the fuel oil, other additives commonly used in the manufacture of explosives.

The expression "petroleum oils" is used herein in a broad sense to include petroleum liquids such as fuel oil, petroleum distillates and liquid petroleum residues, including asphalts.

It will be understood the invention is not limited to the disclosures herein, except as indicated by the appended claims.

What is claimed is:

1. A process of producing detonable mixtures of ammonium nitrate and petroleum oils in regulated proportions such that when detonated the fumes produced are of low toxicity, which process comprises mixing with the petroleum oil a control oil-soluble dyestuff to produce a colored petroleum oil of a definite color, mixing the thus colored petroleum oil containing oil-soluble dyestuff with ammonium nitrate to uniformly distribute the colored petroleum oil throughout the ammonium nitrate and produce a control sample having a predetermined color substantially the same as the color of the desired mixture of ammonium nitrate and petroleum oil in proportions such that when this mixture is detonated fumes of low toxicity are produced, mixing ammonium nitrate with colored petroleum oil having the same dyestuff and in the same relative proportions as in the colored petroleum oil employed to produce said control sample, and regulating such mixing in accordance with the color of the control sample to produce mixtures of ammonium nitrate and colored petroleum oil in which the colored petroleum oil is uniformly distributed throughout the ammonium nitrate and the mixtures have substantially the same color as the color of the control sample, and which mixtures upon detonation result in a gaseous atmosphere of low toxicity.

2. The process as defined in claim 1, in which the petroleum oil is a fuel oil and the ammonium nitrate and colored fuel oil in both the control sample and the desired product are mixed in proportions of from 94.0% to 94.5% by weight of ammonium nitrate and from 5.5% to 6% by weight of fuel oil, the color of the control sample being substantially matched by that of the desired mixture to insure that the amount of fuel oil incorporated therein is within the said range of 5.5% to 6%.

3. The process of producing detonable mixtures of

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ammonium nitrate fuel oil as defined in claim 2, in which the color of the mixture produced by mixing the ammonium nitrate and colored fuel oil is measured by a colorimeter which when the mixture deviates in color from that of the control sample energizes a signal to indicate the deviation from the predetermined color, which signal is employed to control the mixing of the ammonium nitrate and colored fuel oil to produce a mix having proportions of fuel oil and ammonium nitrate within the range of from 94.0% to 94.5% by weight of ammonium nitrate and from 5.5% to 6% by weight of fuel oil, with the fuel oil substantially homogeneously distributed throughout the ammonium nitrate.

4. The process of producing detonable mixtures of ammonium nitrate and petroleum oil in regulated proportions such that when detonated, the fumes produced are of low toxicity, which process comprises utilizing a colored petroleum oil made by mixing petroleum oil with an oil-soluble dyestuff, mixing the thus colored petroleum oil containing oil-soluble dyestuff with ammonium nitrate to uniformly distribute the colored petroleum oil throughout the ammonium nitrate and produce a control sample having a predetermined color substantially the same as the color of the desired mixture of ammonium nitrate and petroleum oil in proportions such that when this mixture is detonated fumes of low toxicity are produced, mixing ammonium nitrate with colored petroleum oil having the same dyestuff and in the same relative proportions as in the colored petroleum oil employed to produce said control sample, and regulating such mixing in accordance with the color of the control sample to produce mixtures of ammonium nitrate and colored petroleum oil in which the colored petroleum oil is uniformly distributed throughout the ammonium nitrate and the mixtures have substantially the same color as the color of the control sample, and which mixtures upon detonation result in a gaseous atmosphere of low toxicity.

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