GOEX CLEAR SHOT

1994 - 2001

A History Of This Black Powder Substitute
Clear Shot Family Tree


1984: Anthony Cioffe, a partner in Golden Powder Company, left the partnership. He then formed Arco Powder which produced a version known as Black Mag Powder for a short period of time. A plant explosion ended that venture.

1987: An explosion at the Golden Powder of Texas, Inc. facility ends this company. Small amounts of powder produced by this Golden Powder of Texas, Inc. reached the market. The powder was quickly withdrawn from the market.

1991: Earl F. Kurtz and Warren Fey (co-inventor) for Legend Products Corporation, Las Vegas, NV. Brett Epstein installed as president of corporation. As a result of an explosion in the plant producing the powder, along with disagreements within the group, the partnership split up.

1992: Warren Fey, after splitting off from Legend Products Corporation, attempts to introduce another version of the ascorbic acid-based powder. This was to be sold by Warren Muzzleloading under the Longrifle Powder name. The project was quickly dropped with no actual powder produced for sale.

1994: Legend Products Corporation, now solely in the hands of Brett Epstein, produces another version of the ascorbic acid-based powder as Black Canyon Powder.

1994: Warren Fey and Ralph Lermayer approach the Elephant Black Powder Company with a scheme to produce a black powder substitute based on a mixture of potassium nitrate and fructose (fruit sugar). Suggesting that this powder could be made on traditional black powder manufacturing machinery at the S/A Pernambuco Powder factory, Recife, Brazil. Nothing came of this proposed project.

1996: GOEX, Inc., Moosic, PA becomes involved in Warren Fey’s fruit sugar-based powder. Small-scale, experimental production is started in a building leased by GOEX, Inc. at an old U.S. Army Ammunition Plant near Camden, Arkansas.

1999: Legend Products Corporation is reformed as Clean Shot Technologies. Producing another version of the ascorbic acid-based powder as Clean Shot Powder. Also begins to produce Clean Shot in pellet form, called Quick Shot.

1999: In December of 1999, GOEX, Inc. begins to ship limited quantities of the fruit sugar-based powder now known as Clear Shot. A bit of a legal battle with Clean Shot Technologies since the respective powders names are similar.

2000: The Hodgdon Powder Company, producer of Pyrodex powder and pellets files suit against Clean Shot Technologies claiming that they (Hodgdon) had a valid patent on the pellet concept and that Clean shot was infringing on this patent.

2001: The Hodgdon Powder Company prevails in their suit against Clean Shot Technologies and is awarded in excess of $1 million dollars in damages. The legal action then moves into punitive damages that could be 3 times the jury award.

2001: GOEX, Inc. at their Minden, LA powder plant, scale up the Clear Shot manufacturing process in the Spring of 2001. On Oct. 31, 2001, a fire and series of explosions destroy the Clear Shot building and production line. This effectively ends the Clear Shot production.

In 1992, the “inventor” of this Clear Shot Powder, Warren Fey, realized that there was little chance that he could get an ascorbic acid based black powder substitute onto the black powder substitute market. The group who had been working with ascorbic acid in the past had played with a large number of chemical combinations. Warren Fey came to feel that the use of fruit sugar would overcome some of the problems that had been encountered with ascorbic acid.

According to Ralph Lermayer, the secret in getting the fruit sugar to work was by borrowing a “trick” from the food industry. A micro-encapsulation process that would negate the hygroscopic properties of the fruit sugar.
A word of caution at this point. To fully grasp the impact of this Clear Shot Powder project on GOEX, Inc.’s business it is necessary to describe the history of this product in detail and the actions of some of those involved in the project. In some cases the information will not be flattering to those involved. Some might consider the information libelous. The author of this paper was at times caught in the middle of all of this in the position of a consultant to one of the parties initially involved. What will be shown is that in this business a product does not always succeed or fail based on its merits. Success or failure will sometimes depend upon the behavior of the individuals involved in the project.

We first hear of this new powder in 1994. Ralph Lermayer contacted the president of the Elephant Black Powder Company, Arlington, TX. A meeting was set up between the owners of the Elephant Black Powder Company and Ralph Lermayer and Warren Fey. The individuals representing the Elephant Black Powder Company were required to sign non-disclosure, or secrecy, agreements.

In my position as a consultant to the Elephant Black Powder Company and the S/A Pernambuco Powder factory, Recife, Brazil, I was informed of this project but not what the powder was actually composed of. When I was told who was proposing this powder I warned the Elephant Black Powder Company that they should not become involved in this project. My advice was ignored.

The president of the Elephant Black Powder Company was then invited to Firearms Development Laboratory in New Mexico. This being the home of Ralph Lermayer with this Firearms Development Laboratory consisting of a back porch on the Lermayer home. The president of the Elephant Black Powder Company was shown some of this new powder and allowed to shoot a few rounds through a rifle with it.

The proposal was that this new powder would be produced on traditional black powder manufacturing machinery at the S/A Pernambuco Powder Factory, in Brazil, where Elephant brand black powder was being produced. Ralph Lermayer and Warren Fey assured the Elephant people that this powder was perfectly safe to make, not nearly as dangerous as the manufacture of black powder. Keep this in mind later on when the production at GOEX is detailed!

When asked why they had approached Elephant and not GOEX the response was that they felt GOEX lacked the necessary level of technical expertise to produce this powder successfully. Another point to keep in mind.

It was not known at that time that in 1995 Warren Fey and Ralph Lermayer lost the right to exploit the ascorbic acid patent. Which explains the switch from ascorbic acid to fructose.
The Elephant Black Powder Company made arrangements for Ralph Lermayer and his wife to fly down to Brazil and spend two weeks at the S/A Pernambuco Powder Factory. The deal being that Ralph Lermayer would later reimburse Elephant, in cash, for his wife’s airfare. Ralph Lermayer was to photograph the black powder plant, write and publish an article on the plant in any USA published black powder journal as his way or repaying his airfare. Neither of which was done after returning to the U.S.

I had raised the question of a patent on this new powder. It was claimed that this new powder could be patented but the papers were never produced. Ralph Lermayer and Warren Fey then failed to communicate with the president of the Elephant Black Powder Company.

In 1996, a rumor began to circulate within the industry that GOEX, Inc. had picked up this powder.

The president of Elephant then informed me as to what this new powder was comprised of. I in turn commented that it could not be patented. Sugar-based powders go back at least 100 years.

So at this point it appeared that the contact with Elephant was little more than a ploy to push GOEX into getting involved in the project. It was at this time that a major change occurred in GOEX. Frank Fahringer had retired as president of GOEX. He had long had no use for any black powder substitute. In 1995 his son took over the leadership of GOEX when Frank Fahringer retired. The son understood that GOEX’s black powder business was in a state of decline and that the black powder substitute might allow GOEX to retain their position in the powder business.

Another point of issue in this was relative to who would finance this venture. Elephant had refused to commit to any large-scale investment. GOEX was at that time owned by an investment group who were themselves reporting to a bankruptcy court. So any investment in this new powder would have to come from outside of GOEX.

The S/A Pernambuco Powder Factory had shown little interest in getting involved in the production of this new sugar-based black powder substitute in 1994. In mid-1995 an event occurred at the black powder plant that insured they would not become involved in any production schemes.

The plant had been producing a sugar-based composition that was being used on the end of safety fuses. This involved mixing sugar and potassium nitrate and then heating it to caramelize the sugar. During the preparation of a batch they had the batch catch fire. This started the building to burn in which it was being processed. While the workers attempted to extinguish this fire there were embers floating over into the section of the plant producing black powder.
A drifting ember landed in a cart of black powder that a worker was trying to push to a safe place. The cart of black powder blew up. This started a series of fires and explosions. By late afternoon the black powder plant was in ruin. Seven workers had been killed and the plant was three quarters destroyed. In addition to the loss of the building and burned worker involved in the sugar-based safety fuse composition initial fire. But this laid to rest the idea that these sugar-based powders are perfectly safe to make.

So in 1996 we hear rumors of GOEX beginning work on the sugar-based powder. Small-scale batches being produced at an old U.S. Army Ammunition Plant near Camden, Arkansas.

Something of an aside in this tale.
Ralph Lermayer was a somewhat well known writer in the gun magazines. GOEX then asked Ralph Lermayer to write a black powder loading manual for GOEX using GOEX black powder. This would be in 1996.
In June of 1997 there was an explosion at GOEX’s Moosic, PA black powder plant. GOEX then closed the plant and terminated the employment of all of the production workers. Construction had been started on a new black powder plant at the old Louisiana Army Ammunition Plant (LAAP) near Minden, LA.
When GOEX began production at the Minden Plant in early 1998 the powder was not the same as that produced at the now abandoned Moosic, PA plant. So Ralph Lermayer had to repeat all of the ballistics testing using Minden production.
Then there was something of a falling out between the president of GOEX and Ralph Lermayer. The GOEX bp loading manual had progressed as far as preparation for publication but was never published. That was $20 to $30 thousand dollars wasted. It also ended any connection with Clear Shot and Ralph Lermayer.

So small-scale production proceeded at Camden, Arkansas.

GOEX had started to advertise this new black powder substitute in 1997, promising its introduction in 1998. Finally in December of 1999 GOEX made the first shipment of Clear Shot to dealers in very limited quantities. This shipment represented at least one year’s small-scale batch production.
It wasn’t until early 2001 when GOEX finally had a full-scale production line set up at the Minden, LA plant to produce Clear Shot in volume quantities.
So by the Spring of 2001 GOEX is running full page magazine adds featuring the Clear Shot powder. With production on a large scale.
Disaster Strikes!

Dayline plant explosion hurts 2
Donelle Pea / The Times
Posted on November 1, 2001

DOYLINE - Multiple explosions at Goax Inc., a black powder-manufacturing company in a former ammunition plant in Webster Parish, left two people injured and other employees shaken Wednesday afternoon. Early estimates put damage at the plant at $2.5 million.

The incident is the third at the 29-acre plant at Dayline in the past three years. An employee was burned severely in a flash fire and explosion Jan. 25, 2000. And an explosion Nov. 5, 1999, killed a worker.

Occupational Safety and Health Administration inspectors are expected on site today to begin looking into Wednesday's incident. State police are investigating to determine if it was caused by human error.

"We don't know what set it off at this time," Senior Trooper Steve Childress said. "The follow-up investigation will be multifaceted, involving the state police, Alcohol Tobacco and Firearms agents and OSHA."

State police received the first call of an explosion Wednesday at 1:25 p.m., Childress said. It happened in a room where employees were in the initial stages of mixing Cleanshot, a synthetic black powder used by muzzle loaders. Six employees were in the first building, known as the H line. They and 36 other employees were evacuated from the area.

"I was just performing my job, and the next thing I heard was a boom, the line just went up in smoke," said employee John Montgomery, who was working in an area near the explosion. "Everybody was rushing out."

Company representatives told state police they anticipated a second explosion. It came at 2:47 p.m., with 1,000 pounds of Cleanshot detonating.

Childress said authorities are unsure how many pounds exploded the first time, but the amount was less than the second. A series of three or four other "very small" explosions followed.

Two employees in the building where the first explosion occurred were treated for minor injuries. One was treated on site by ambulance personnel for what appeared to be shock, state police said. The second was taken to the hospital and treated for abrasions and bruises.

Montgomery said this is the first time during his three years at the plant to witness an explosion. "This is just something I have to deal with. It's a fear you learn to live with."

Vickie Welborn contributed to this report.
Remember the claim that this sugar-based powder is perfectly safe to manufacture?
Above we have the notice of inspection found on the OSHA web site in the “Establishment Search Inspection Detail – Public View” section. Note the company name, “Goex Clear Shot Powder Company”. Since all of the investment capital for Clear Shot powder came from outside GOEX, Inc’s investment company owners, it was necessary to set up the Clear Shot as another company.
Points of interest from the newspaper articles (on-line edition).

1. 6 employees in the building. Two with minor injuries. (One suffered bruises from bumping into obstacles in his flight.)

2. The fire burned from 1:25 p.m. until 2:47 p.m.

3. Multiple small explosions. The explosion (“detonation”) of 1000 pounds of finished powder.

4. Estimated loss set at $2.5 million.

A number of things may be deduced from this information.

1. OSHA has repeatedly cited GOEX for having aisles leading to building or emergency exits blocks or partially obstructed. That is again a distinct possibility here.

2. Clearly there was no operating fire suppression system in the building at the time.

3. Finished powder was being allowed to accumulate at the finished powder end of the production line.

4. The building and production machinery were a total loss.

As it stands now. There are no plans to rebuild the Clear Shot production line. Remember that this Clear Shot production line went into operation earlier in 2001. The month of March has been stated. If there was any type of fire insurance coverage on the production line the insurance company would not honor any policy when the line was being operated unprotected by a fire suppression system. So the outside investors lost all of their investment due to GOEX management taking a calculated risk. Most likely after having believed the notion that this product was much safer to make, compared to black powder manufacture. Would the original outside investors come up with the $3 to $4 million dollars that would be required to replace the machinery lost on Oct. 31, 2001. Not likely!

It will be another month or two before OSHA posts the list of safety violations they found during their inspection of the rubble on Oct. 1, 2001.

It appears at this time that the Clear Shot line will not be rebuilt and therefor that is the end of Clear Shot powder.
From the GOEX web site on 12/19/99.
What was Clear Shot - What was claimed for it - In actuality

From the GOEX web site claims.

“Brand New Concept in Propellants - does not contain ascorbic acids or perchlorates.”
This is of course aimed at Clean Shot Technologies “Clean Shot Powder” (ascorbic acid) and Hodgdon’s Pyrodex (perchlorates).

“Clean Burning - produces very little residue and does not build up from shot to shot!”
Most shooters thought that Hodgdon’s Pyrodex was a clean-burning black powder substitute as long as they shot patched balls or lead conicals. When the plastic sabots came along for in-line action rifles the view changed dramatically. With the plastic sabots, shooters found that they had to swab the bore after two or three shots in order to load the next sabot.

“Non-Corrosive - contains nothing that will corrode the gun barrel!”
This is of course directed at Pyrodex with its high potassium perchlorate content. Pyrodex long being noted for extensive corrosion in gun barrels not properly cleaned and the micro-pitting of those that were given a good cleaning.

“Non-Hygroscopic - does not pick up moisture, even in very high humidity areas!”
Pyrodex is at least twice as hygroscopic as a good black powder. The ascorbic acid based powders ranged from very hygroscopic on up to deliquescent.

“Indefinite Shelf Life - does not deteriorate or become unstable over time!”
This is the most accurate of the claims that were made for Clear Shot. Clear Shot being little more than a compounded mixture of caramelized fruit sugar and potassium nitrate. Both the ascorbic acid powders and Pyrodex suffered shelf-life problems whenever the powders were allowed to pick up even small amounts of moisture from the air.

“Consistent Velocities - designed like authentic black powder, low standard deviations!”
This is partly correct, depending on what you were using the powder for. In hunting situations the shot to shot performance was on par with black powder. In long-range competition shooting the Clear Shot still could not match a good black powder in accuracy.
Clear Shot was little more than a modification of various sugar-based powders that date back into the late 19\textsuperscript{th} century. The “modern” approach being mainly the idea of producing the powder from a slurry, rather than from a melted, molten state, using up to date candy making machinery.

With the candy making machinery, using a slurry, the resulting grains become nearly spherical in shape. The grains are then given a graphite coating.

In the photo on the left the grains of Clear Shot were gently rolled between pieces of 400 grit wet or dry sandpaper to remove the graphite surface coating. The color of the partially caramelized fruit sugar then shows.
In a flintlock rifle.

Attempts to use the Clear Shot in a flintlock rifle showed, again, that when a black powder substitute exhibits an ignition temperature, or combustion properties, that permit it to be shipped as a flammable solid, rather than as an explosive, it will not work in a flintlock without resorting to the use of black powder as a lock prime.

When the Clear Shot powder was used as a lock prime it would ignite every time the lock was cycled and threw sparks. But at no time would the flash from the pan ignite the Clear Shot used as a main charge in the barrel. As soon as black powder would be used in the lock pan, the main charge would ignite reliably. Unlike Pyrodex, Clear Shot did not require that the breech first be primer with a small amount of black powder in order to give a fast and reliable ignition of the main charge of Clear Shot. So in this respect the Clear Shot was superior to Pyrodex in a flintlock ignition arm.

Moisture content of the powder from the can.
Oven temperature 150 F until constant weight of sample.
0.3%, Elephant 3Fg, Lot 058, Date Code 25/99
0.7%, GOEX Clear shot, 3Fg, 33-01, 98NO04B
0.8%, GOEX Clear Shot, 2Fg, 22-01, 98NO04B
(Nothing out of the ordinary in this data.)

Hygroscopic behavior.
Powder samples to be tested are placed in the oven at 150 F until constant weight, assumed to be total dryness.

At 69% Relative Humidity.
0.4% increase, 2 hours, Elephant 3Fg, Lot 058, Date Code 25/99.
1.3% increase, 2 hours, GOEX Clear Shot 3Fg, Lot 98NO04B.

At 100% Relative Humidity.
0.6% increase, 1 hour exposure, Elephant 3Fg, Lot 058, Date Code 25/99.
1.0% increase, 2 hour exposure, Elephant 3Fg, Lot 058, Date Code 25/99.
1.0% increase, 3 hour exposure, Elephant 3Fg, Lot 058, Date Code 25/99.
1.5% increase, 5 hour exposure, Elephant 3Fg, Lot 058, Date code 25/99

1.1% increase, 1 hour exposure, Clear Shot 3Fg, 98NO04B.
1.5% increase, 2 hour exposure, Clear Shot 3Fg, 98NO04B.
1.8% increase, 3 hour exposure, Clear Shot 3Fg, 98NO04B.
3.0% increase, 5 hour exposure, Clear Shot 3Fg, 98NO04B.

The data shows that Clear Shot is roughly twice as hygroscopic, compared to black powder. Pyrodex data would be 3 times that of black powder and Clean Shot far above both of them.
Loading Density.

1.0 g/cc, GOEX Clear Shot 3Fg.

This loading density figure matches the loading density for GOEX black powder in the same grain size. This means that this Clear Shot is a weight to weight or volume to volume replacement for GOEX black powder. At the same time, the Clear Shot was formulated to give a ballistic strength equal to that of GOEX black powder. That ballistic strength representing what would be known as a rifle burn rate black powder.

Ballistics data.

Test rifle: Lyman Trade Rifle, .50 caliber, percussion ignition.
Speer .490" balls, .020" #40 cotton drill patching, Lehigh Valley lube.
CCI #11 Magnum percussion caps.
Pact Professional Chronograph.
80 grain volume charges.
Bore wiped between shots.
35 degrees F, 50% R.H.

1554 fps ave., ES 51 fps, Elephant 3Fg, Lot 058, Date Code 25/99
1669 fps ave., ES 61 fps, GOEX Clear Shot 3Fg, 33-01, 98NO04B

1534 fps ave., ES 52 fps, Elephant 2Fg, Lot 045, Date Code 25/99
1513 fps ave., ES N/A, GOEX Clear Shot 2Fg, 22-01, 98NO04B (only two rounds fired)

When these two samples of Clear Shot were test fired in the .50 caliber Lyman GPR flintlock, the powders left a considerable amount of black material in the bore. A mixture of unburned carbon and some melted sugar.

In the percussion ignition rifle these samples of Clear Shot quickly became difficult to deal with. While shooting the 3Fg Clear Shot the flash channel between the base of the nipple and the powder chamber in the breech became packed solid with the combination of unburned carbon and melted sugar. In attempting to fire the fourth round in the series it was necessary to first remove the nipple and dig the residue out of the flash channel. After that, this had to be done before every shot. The 2Fg would fill the channel with each shot. The shooting was then abandoned. This certainly represented no improvement over the use of black powder in the gun considering 30 to 50 shots with black powder before such an event would happen.
The results reported were obtained with powder that its makers claimed was a very good powder. The best black powder substitute ever made.

Since by 1999 this project had sort of staggered along without turning a profit the process of making the powder was speeded up with a few short cuts in the process. Clear Shot produced in 2000 proved to be considerably slower in the same gun as a result. The rifle burn rate seen in the first release of Clear Shot fell to that of a musket burn rate black powder. For some unknown reason this reduced the amount of unburned carbon seen in the gun with the Dec. 1999 released powder but increased the amount of melted, unburned sugar in the bore. This left patches of fouling in the bore that were difficult to remove with wet patches and degraded accuracy with the gun.

This “program” of cutting corners in the Clear Shot processing continued in 2001 until the end of production on Nov. 31, 2001.

This Clear Shot powder had the potential to become a good, reliable replacement for black powder in certain types of guns used for hunting. It is doubtful if a shooter would win any serious target shooting events with it. Rather than perfect the powder to a more reliable state, the drive was to increase production quantities to make a greater amount of profit from it. In the end, the drive to increase profits resulted in the demise of the product.
Ballistic strength comparison to other powders at the time.

Test rifle: 
.50 caliber Lyman Trade Rifle, percussion ignition with a 28" barrel. 
.490 Speer balls, .018" #40 cotton drill with Lehigh Valley lube. 
CCI #11 Magnum caps. 
Pact Professional Chronograph 15 feet from the muzzle. 
Powder measure by volume, Treso adjustable throwing 100 grains weight of water at the 100 setting on the sliding stem.

80 grain charges.

**3F granulation size powder samples.**

1669 fps ave. GOEX Clear Shot, 98NO04B (First release)

1536 fps ave. GOEX 01NO13B (2001 - Nov. - 13th packing date)
1426 fps ave. GOEX 01NO14B (2001 - Nov. - 14th packing date)
1490 fps ave. GOEX 02AU01B (2002 - Aug. - 1st)
1663 fps ave. GOEX 02SE10B (2002 - Sept. - 10th)
1582 fps ave. Elephant, Lot 058, Date Code 25/99
1364 fps ave. Lidu (Chinese, sold by Corman’s in 1999)
1860 fps ave. Swiss, 2002 production in plastic bottles.

**2F granulation size powder samples.**

1513 fps ave. GOEX Clear Shot, 98NO04B (First release)

1792 fps ave. Triple Seven, 2002 production.
1371 fps ave. GOEX 99NO03B (1999 - Nov. - 3rd)
1553 fps ave. KIK, 2000 production (imported by GOEX)
1540 fps ave. Elephant, Lot 045, Date Code 25/99
1667 fps ave. Swiss 1997 production. (Tin cans)
1699 fps ave. Swiss 1999 production. (Tin cans)
1658 fps ave. Swiss 2001 production. (Tin cans)
1763 fps ave. Swiss 2002 production. (Plastic bottle, deliberate increase in velocity)
Title: Fuel and explosive composition with ferric or cupric ion and reducing sugars.

Abstract: This invention relates to fuels used in explosive, pyrotechnic, gas generating, and propellant compositions. The fuel composition of the present invention comprises the reaction products formed as a result of reacting a transition metal or transition metal compound, preferably ferric nitrate or ferric hydroxide with a reducing sugar. The fuel composition of the present invention is suitable for use in explosive compositions by mixing with an oxidizing agent. The fuel composition of the present invention and explosive compounds derived therefrom exhibit non-fouling and non-corrosive properties when used in firearms, along with greatly reduced residue.

Inventors:
Fey, Warren O. (11092 E. Harvard Dr., Aurora, CO. 80014)
Application Number: 08/055545 Filing Date: 05/03/1993 Publication Date: 11/14/1995

Assignee: Maschinenfabrik Goebel GmbH (DE)

Primary Examiner: Nelson, Peter A. Attorney, Agent or Firm: Cox, Ray F.

Claims: What is claimed is:

1. A fuel composition comprising:
   (a) The reaction products of Fe(NO3)3.9H2 O and a sugar selected from the group commonly known as reducing sugars, and
   (b) Degradation products of a sugar, and
   (c) Any remaining unreacted sugar.

2. A fuel composition as defined in claim 1 wherein the Fe(NO3)3.9H2 O and the sugar are supplied in a molar ratio of up to 3:23.

3. A binder for use in explosive compositions comprising:
   (a) The reaction products of Fe(NO3)3.9H2 O and a sugar selected from the group commonly known as reducing sugars,
   (b) Degradation products of a sugar, and
   (c) Any remaining unreacted sugar.

4. A binder as defined in claim 3 wherein the Fe(NO3)3.9H2 O and the sugar are supplied in a molar ratio of up to 1:1.
5. A fuel composition comprising:
(a) the reaction products of a compound of a transition metal ion selected from the group consisting of ferric ions and cupric ions and a sugar selected from the group commonly known as reducing sugars,
(b) degradation products of the sugar, and
(c) any remaining unreacted sugar.

6. The fuel composition of claim 5 wherein said transition metal ion is a ferric ion.

7. The fuel composition of claim 6 wherein the weight ratio of ferric ion to sugar is up to 3:100.

8. The fuel composition of claim 6 wherein said compound of a transition metal ion is Fe(NO3)3.9H2 O.

9. The fuel composition of claim 8 wherein the Fe(NO3)3.9H2 O and the sugar are in a molar ratio of up to 3:23.

10. The fuel composition of claim 6 wherein said compound of a transition metal ion is Fe(OH)3.

11. A binder for use in explosive compositions comprising:
(a) the reaction products of a compound of a transition metal ion selected from the group consisting of ferric ions and cupric ions and a sugar selected from the group commonly known as reducing sugars,
(b) degradation products of the sugar, and
(c) any remaining unreacted sugar.

12. The binder of claim 11 wherein said transition metal ion is a ferric ion.

13. The binder of claim 12 wherein the weight ratio of ferric ion to sugar is up to 3:100.

14. The binder of claim 12 wherein said compound of a transition metal ion is Fe(NO3)3.9H2 O.

15. The binder of claim 14 wherein the Fe(NO3)3.9H2 O and the sugar are in a molar ratio of up to 3:23.

16. The binder of claim 12 wherein said compound of a transition metal ion is Fe(OH)3.
17. An explosive composition comprising an oxidizer in admixture with a fuel composition comprising:
(a) the reaction products of a compound of a transition metal ion selected from the group consisting of ferric ions and cupric ions and a sugar selected from the group commonly known as reducing sugars,
(b) degradation products of the sugar, and
(c) any remaining unreacted sugar.

18. The explosive composition of claim 17 wherein said transition metal ion is a ferric ion.

19. The explosive composition of claim 18 wherein the weight ratio of ferric ion to sugar is up to 3:100.

20. The explosive composition of claim 18 wherein said compound of a transition metal ion is Fe(NO3)3.9H2 O.

21. The explosive composition of claim 20 wherein the Fe(NO3)3.9H2 O and the sugar are in a molar ratio of up to 3:23.

22. The explosive composition of claim 18 wherein said compound of a transition metal ion is Fe(OH)3.

23. The explosive composition of claim 19 wherein said oxidizer is selected from the group consisting of nitrates, chlorates, perchlorates, permanganates, and peroxides.

24. The explosive composition of claim 23 wherein said oxidizer is ammonium nitrate.

25. The explosive composition of claim 23 wherein said oxidizer is potassium nitrate.

26. The explosive composition of claim 25 wherein the weight ratio of the fuel composition to the potassium nitrate is from about 20:80 to 50:50.

27. The explosive composition of claim 21 wherein said oxidizer is selected from the group consisting of nitrates, chlorates, perchlorates, permanganates, and peroxides.

28. The explosive composition of claim 27 wherein said oxidizer is ammonium nitrate.

29. The explosive composition of claim 27 wherein said oxidizer is potassium nitrate.

30. The explosive composition of claim 29 wherein the weight ratio of the fuel composition to the potassium nitrate is from about 20:80 to 50:50.
31. The explosive composition of claim 22 wherein said oxidizer is selected from the group consisting of nitrates, chlorates, perchlorates, permanganates, and peroxides.

32. The explosive composition of claim 31 wherein said oxidizer is ammonium nitrate.

33. The explosive composition of claim 31 wherein said oxidizer is potassium nitrate.

34. The explosive composition of claim 33 wherein the weight ratio of the fuel composition to the potassium nitrate is from about 20:80 to 50:50.

FIELD OF THE INVENTION
This invention relates to fuels used in explosive, pyrotechnic, gas generating, and propellant compositions. More specifically, this invention finds particular, but not exclusive, utility in compositions intended to replace Black Powder in all its applications.

BACKGROUND OF THE INVENTION
Explosive compositions must comprise a fuel and a source of oxygen. Oxygen is frequently supplied by nitrates, chlorates, permanganates, peroxides and other oxidizers, both organic and inorganic, known in the art. The fuel should comprise materials that can theoretically be oxidized completely and rapidly. Ideally, there should be very little residue remaining after the reaction takes place, with as much of the original material as possible being converted to heat energy and gases. It is known in the art that the characteristics and performance of an explosive composition can be significantly altered by the use of various oxidizers, as well as various amounts of the oxidizer component, while the fuel component remains unchanged and, of course, vice-versa.

The primary examples of this type of composition are Black Powder and "Pyrodex". When Black Powder is burned, approximately 56% of the total weight remains as solid material. As is known to persons who use Black Powder in firearms, this residue causes fouling of the barrel, and repeated, unpleasant cleaning of the firearm. Many times the barrel must be swabbed out between shots. The presence of sulfur in Black Powder results in combustion products which, when combined with atmospheric moisture, cause corrosion of the barrel. While "Pyrodex" causes less fouling, it not only contains sulfur, but also contains potassium perchlorate, which results in the formation of soluble chloride salts. These salts are also corrosive to the barrel.

Historically, sucrose is known as a component of pyrotechnic compositions. Attempts have been made to produce gunpowder from sucrose and potassium chlorate, with unpredictable and disastrous results. Timmerman discloses, in U.S. Pat. No. 3,862,866, the use of sucrose and potassium chlorate in gas generating compositions. The sucrose is used in an unmodified and unreacted form; i.e., no degradation products are used. Other explosive compositions have been formulated which exhibit improved safety, performance, and other improved characteristics. These are described in the following U.S. Pat. Nos.: 4,497,676 - Kurtz Gunpowder Substituted Composition and Method 4,728,376 - Kurtz Explosive Composition and Method 4,881,993 - Furbringer et al.
Fuel and Explosive Composition and Method of Making Same

The explosive compositions disclosed in these patents consist primarily of an organic acid fuel, usually ascorbic or erythorbic acid, and an inorganic nitrate oxidizer, usually potassium nitrate. While these compositions exhibit varying degrees of performance, they commonly exhibit non-fouling and non-corrosive properties when used in firearms, along with greatly reduced residue. The major drawback common to all the compositions disclosed in the above referenced U.S. patents is the cost of raw materials, and the instability of the raw materials market. In addition, many of these compositions exhibit unacceptable levels of hygroscopicity.

It is the principal object of the present invention to produce a fuel composition for use in explosive compositions. Such fuel exhibits improved performance, excellent binding and adhesive properties and greatly reduced cost and stability of the raw materials market. It is a further object of the present invention to produce a fuel composition well suited for use as a binder and or modifier in explosive, pyrotechnic, and propellant compositions. It is a still further object of the present invention to produce an explosive composition comprising an improved fuel composition and an oxidizing agent. It is a further object of the present invention to use such improved fuel composition to form an explosive composition, which, when utilized as a gunpowder, evidences improved performance, including improved burn characteristics, with less residue, and producing greater velocities at pressures comparable to those produced by Black Powder and other existing gunpowder substitutes. A related object is to provide a method for making an improved fuel composition and a method for making an explosive composition in a safe and extremely cost effective manner, said explosive composition having the foregoing character and containing an improved fuel composition.

SUMMARY OF THE INVENTION

A significant aspect of the present invention relates to fuels formed from reducing sugars as a consequence of their ability to reduce many transition metal ions. When reacted with warm Fehling's solution a reducing sugar produces a red precipitate. The precipitate consists of a red copper oxide formed as a result of the reduction of the copper ions present. This is a standard test, used in the medical field, for the presence of glucose.

Another significant and specific aspect of the present invention relates to a fuel formed as a result of a reaction of reducing sugars, and/or their degradation products, with an iron compound, the iron contained therein occupying a state that is capable of further reduction, such as the reduction from Fe ++ to Fe +. Yet another significant aspect of the present invention relates to a class of binders/modifiers suitable for use in explosive compositions.
formed as a result of reactions between reducing sugars and a transition metal or transition metal compound.

Another significant aspect of the present invention relates to an explosive composition comprising an oxidizing agent and the fuel formed as a result of reactions between a reducing sugar and a transition metal or transition metal compound, preferably iron or an iron compound. A further significant aspect of the present invention relates to a method for making a fuel suitable for use in an explosive composition by forming reaction products of reducing sugars and iron or iron compounds. A still further significant aspect of the present invention relates to a method for making an explosive composition by forming a fuel, comprising the reaction products of reducing sugars and an iron compound, degradation products of reducing sugars, and any remaining unreacted sugars, and mixing the fuel with an oxidizing agent.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The fuel composition of the present invention comprises the reaction products formed as a result of reacting a transition metal or transition metal compound, preferably ferric nitrate or ferric hydroxide with a reducing sugar. It should be noted at this point that, although sucrose is not classed as a reducing sugar, it can be used as a raw material by merely subjecting it to a simple inversion process. A number of these processes are well known in the sugar industry. The use of different sugars or blends of sugars will provide different performance characteristics in the end product. The fuel may be prepared in an aqueous solution with the weight of Fe(NO₃)₃ • 9H₂O being approximately equal to 10% of the weight of the sugar. Such aqueous solution is evaporated at a temperature of 100°C - 110°C. The dried black residue produced comprises the reaction products which constitute the improved fuel composition of the present invention. A 3% solution of H₂O₂ may be used in place of water.

A stoichiometric quantity of base may be added to the solution to alter the pH of the solution and cause the production of Fe(OH)₃ pursuant to the following reaction:

Fe(NO₃)₃ • 9H₂O + 3KOH → Fe(OH)₃ + 3KNO₃ + 9H₂O

The presence of ferric hydroxide is desirable in this application due to the fact that these sugars are substantially degraded by the action of bases and the presence of degradation products is desirable. The resultant black color of the fuel is dependent either on the result of the reduction of the Fe³⁺ ions and the subsequent colloidal particle oxide formation, which has the added advantage of being an excellent combustion catalyst, or the reaction of iron ions with phenol compounds produced as a consequence of the degradation of the sugars. This reaction is well known in the food industry.

The choice of the base used is dependent on the desired end use of the product. For instance, an acceptable product can be produced by the use of NH₄OH in place of KOH. However, this results in ammonium nitrate being included in the final product. In many applications this is acceptable, but if the product is intended to be used as a propellant contained in brass cartridges, the ammonium nitrate can react with the copper present in the brass, forming tri-amino cupric nitrate. This is a sensitive, initiating explosive similar in activity to lead styphnate priming compound and is not desirable as a component of a
propellant composition. The fuel composition thus produced has excellent adhesive properties and is suitable for use as a binder in explosive compositions. Adhesives produced by the reaction of sugars with metal compounds are known in the sugar industry. The term "binder" as used herein, includes binders and modifiers. The explosive composition of the present invention comprises a mixture of an oxidizing agent, preferably a nitrate-containing inorganic oxidizer such as potassium nitrate, and the improved fuel of the present invention. The explosive composition thus produced has substantially enhanced physical and performance characteristics as well as very low cost. Laboratory methods used to obtain the improved fuel composition and the improved explosive composition are described below in Examples I through V. Methods used to obtain the improved fuel composition and the improved explosive composition which may be employed on a larger scale are described below also in Examples I through V.

EXAMPLE I

Approximately 100 grams of a reducing sugar, preferably fructose, are added to a 3% solution of H₂O₂ so as to create a saturated solution. A non-reactive vessel should be used, preferably glass or plastic. Approximately 10 grams of an Fe⁺⁺ compound, preferably Fe(NO₃)₃·9H₂O, are added to the solution, producing an amber colored solution. While stirring, slowly add 30% solution of H₂O₂ only until solution becomes colorless. The solution is then heated until the water is driven off and the temperature rises to 225°F. Drying is continued in an oven at 225°F until a dark brown or black friable mass is formed. The material produced in this manner is suitable for use as the fuel component in explosive and/or deflagrating compositions. The fuel may be ground by any method which will yield the desired particle size. Those skilled in the art will appreciate that the performance characteristics of the end product are extremely dependent on the particle size. In this laboratory method, a small ball mill is used, and the desired particle size is on the order of 10 microns. When the fuel composition is to be used as a binder or modifier, the iron compound or other transition metal compound may be used in a ratio of up to an amount that is equimolar with the amount of the reducing sugar used. To produce an improved explosive composition, the improved fuel and the oxidizer component, are mixed together in approximately stoichiometric amounts, based on the formula of the original sugar used. When KNO₃ is used as the oxidizer, the ratio of oxidizer to improved fuel composition is approximately 2:1 by weight. As is known in the art, differing performance characteristics desirable for different uses may be obtained by adjusting this ratio. As is also known in the art, the weight ratios will vary according to the type of oxidizer used. The mixing may be accomplished by any method suitable. In this laboratory procedure, the fuel and oxidizer components are ground separately in ball mills, either dry or in an ethanol slurry, and then thoroughly mixed. The fuel composition should not be triturated with chlorates, or any similarly sensitive oxidizing material. The explosive composition may be granulated and dried using any one of many techniques known in the art. In this method, the thoroughly mixed, dried components are slightly moistened and granulated and polished by tumbling or vibration. Any number of devices
known to the candy industry will also fulfill this requirement. The polished granules should then be thoroughly dried and classified for size. With this fuel composition, a heat cure of approximately 225°F is beneficial in terms of increasing the granular integrity and driving off any residual moisture.

EXAMPLE II
A fuel composition and an explosive composition similar to those obtained with the laboratory method described in Example I may be produced by preparing a saturated solution of sucrose in H\textsubscript{2}O\textsubscript{2}, adding Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O in an amount equal to approximately 10% of the weight of the sucrose and allowing the solution to sit for approximately 48-72 hours. The acidic condition causes partial inversion of the sucrose. Complete inversion of sucrose yields equimolar portions of glucose and fructose, both of which are reducing monosaccharides.

From this point forward the method set forth in Example I should be followed.

EXAMPLE III
An improved explosive composition suitable for use as a detonating compound may be produced by substituting ammonium nitrate or a mixture of ammonium nitrate and potassium nitrate in place of potassium nitrate as the oxidizing agent of Examples I and II. Those skilled in the art will appreciate that the substitution of other oxidizing agents, such as the various chlorates, perchlorates, perborates, and permanganates, for example, for potassium nitrate as the oxidizing agent will also result in an improved explosive composition.

The suitability of the improved explosive composition as a deflagrating, detonating, pyrotechnic, propellant, gas generating, or other type of explosive composition will depend, in part, on the choice of the oxidizing agent. Moreover, an appropriate ratio of fuel composition to oxidizing agent will vary depending upon the particular oxidizing agent employed and the stoichiometric relationships among the explosive composition constituents. For example, while a satisfactory weight ratio of improved fuel composition to potassium nitrate is approximately from 20:80 to 50:50, a preferable weight ratio of improved fuel composition to ammonium nitrate is approximately from 5:95 to 25:75. The use of sucrose syrup with ammonium nitrate is disclosed in U.S. Pat. No. 4,427,465.

EXAMPLE IV
Prepare a solution of sugar, H\textsubscript{2}O\textsubscript{2}, and Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O as described in Examples I and II. While stirring, add a stoichiometric amount, with respect to the amount of FE(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O, of NH\textsubscript{4}OH solution until the solution turns dark brown. If any ammonia odor remains after a few minutes, there is an excess of NH\textsubscript{4}OH and the quality of the fuel is diminished. The drying time of the fuel is slightly longer. This approach takes advantage of the non-enzymatic browning reactions, known as the Maillard reaction, well known in the food industry. In standard practice, in the food industry, amino acids are reacted, at elevated temperatures, with sugars. This procedure results in the formation of
nitrogen containing, sugar-based compounds, as well as other degradation products of the sugar used. In non-food uses, many other amino compounds may be used in place of the amino acids. However, the inclusion of these products generally causes objectionable odors during manufacture and end use of the product, as well as an unnecessary increase in cost. Additionally, as discussed previously, the ultimate inclusion of ammonium nitrate in the end product becomes a possibility. In end uses where exposure to copper is likely, this is not desirable. Ammonium nitrate is also quite hygroscopic and therefore is also undesirable in many applications.

EXAMPLE V
Prepare the solution as described in example I. While stirring, add KOH solution. The molar ration of KOH to Fe(NO$_3$)$_3$·9H$_2$O should be approximately 3:1. A reaction takes place which produces Fe(OH)$_3$ and KNO$_3$. The Fe$^{3+}$ is presumably reduced to Fe$^{2+}$ and the formation of FeO results. The FeO formed in this manner occurs in very small particle size, presumably colloidal, and functions as a combustion catalyst in addition to degrading the sugar as the Fe$^{3+}$ is reduced to Fe$^{2+}$. This solution is then treated in the same manner as the solution in Example I to obtain an improved fuel composition. Again, the presence of the various degradation products of the sugar(s) is a very important element of the improved fuel composition. The formation of the degradation products is primarily affected by pH, temperature, and time. The type of product is primarily affected by pH. The rate of reaction is primarily affected by temperature, and the quantity of degradation products is primarily affected by time, when the other factors remain constant. In the case of degradation products produced by reacting the sugar(s) with other compounds, such as oxidizing agents, the nature of the degradation products is affected by the nature of the other compounds.

While the reducing sugars are able to reduce many other metallic ions, as well as iron, iron is preferred, based on cost, availability, and relative lack of toxicity. It is understood that other transition metal ions, such as copper, will fulfill the function performed by the iron, with consequent variations in characteristics and performance. The reduction, by the reducing sugars, of various metal ions is well known, and has been studied extensively in the sugar industry.

Presently preferred embodiments of the present invention have been described. It should be understood that this description has been made by way of preferred examples, and that the invention is defined by the scope of the following claims.