

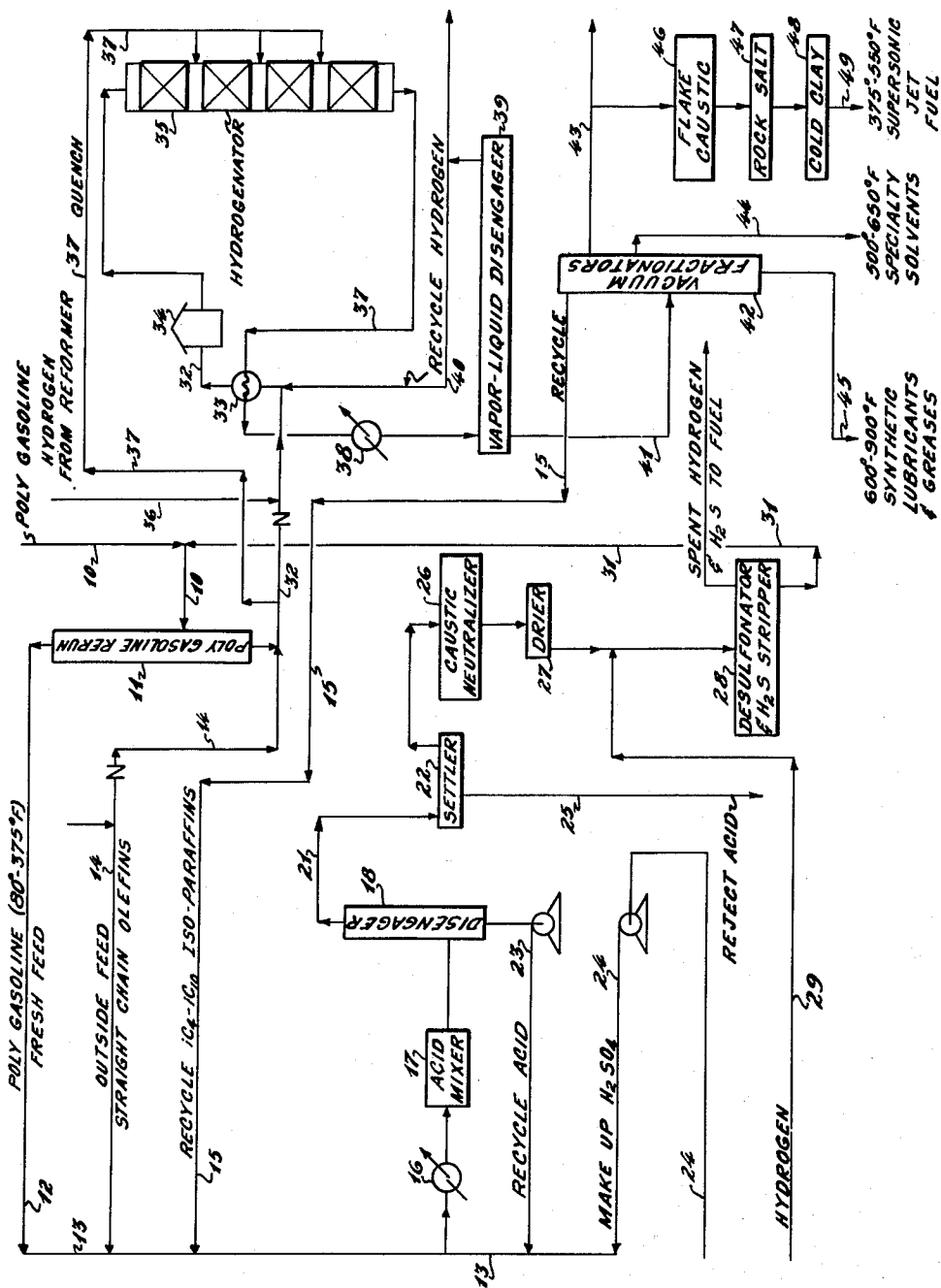
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PROCESS FOR THE PRODUCTION OF SUPERSONIC JET FUELS

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PROCESS FOR THE PRODUCTION OF
SUPERSONIC JET FUELS

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This invention relates to a process for producing hydrocarbon fuels for supersonic jet aircraft. More specifically, it relates to a process for producing fuels comprising mixtures of saturated aliphatic compounds having more than eleven carbon atoms per molecule from polymer gasoline.

Many different types of hydrocarbon fuels have been produced to meet the increasingly rigid requirements imposed by modern aircraft. These fuels have included naphthenics, alkylnaphthenics, paraffins, and isoparaffins having different degrees of branching, as well as mixtures of such components.

The development of Mach 3 jet aircraft has presented a need for a new type of fuel which must meet even more rigid specifications. Among other requirements, fuels for such aircraft must display a high heating value per unit weight, low freezing point, low viscosity at low temperatures, low vapor pressure at elevated temperatures, and high specific heat.

In addition, one of the most important criteria for a supersonic jet fuel is its so-called research coker test rating. This rating is indicative of the thermal stability of the fuel. Fuel stored in the wing tanks of a supersonic aircraft is utilized as a heat sink to absorb heat from the surface of the wing, whereby the rise in wing temperature caused by skin friction at supersonic speeds is minimized. Under typical conditions the fuel may be subjected prior to combustion to temperature in excess of 500° F. for several hours. At such temperatures impurities in the fuel, or even the fuel itself, may decompose or react to form undesirable compounds which impair its combustion properties or cause improper operation of the engine or both. The research coker test, which is well known in the industry, measures the thermal stability of a supersonic fuel by subjecting it to conditions generally simulating the adverse conditions to which it is subjected in use. In accordance with this test, the fuel is heated in a reservoir to a temperature which corresponds to the temperature of fuel in the aircraft wing tanks. From the reservoir the fuel is pumped through a preheater tube at a higher temperature, corresponding to the temperature in the inlet manifold of the jet engine, to a second heater and then through a filter which removes non-liquid particles formed during the test. The operating conditions of the test can be varied over a range as follows:

Pumping flow rate, lbs./hr.	2-10.
Preheater temperature, ° F.	Ambient-800.
Filter temperature, ° F.	500-900.
Pumping pressure, p.s.i.g.	250.
Duration of run, hrs.	5-15.

Results of the research coker test are expressed in terms of a rating indicating relatively the quantity of deposit left in the preheater, ranging from 0 (best) to 8 (worst), and in terms of the pressure drop, in inches of mercury, across the filter, ranging from 0 (best) to 25" (worst). The extremely high thermal stability demanded of supersonic jet fuels is indicated by the fact that they must have a preheater deposit rating no higher than 2 and a filter pressure drop no greater than 5 inches.

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Still another important criterion for a supersonic jet fuel is its luminometer number. The luminometer test measures the relative brightness of the flame produced by a burning hydrocarbon fuel, which is an indication of the average degree of branching of the compounds constituting the fuel. The result of this test is expressed by reference to an arbitrary scale, high luminometer number indicating low average branching.

In order to define for fuel producers the several requirements which a hydrocarbon fuel must meet to be satisfactory as a supersonic jet fuel, the following specifications have been established by the aviation industry.

Net heating value, B.t.u./lb.	18,900 min.
Freezing point, ° F.	-30 max.
Luminometer number	100 min.
Viscosity, cs. @ -30° F.	15 max.
Vapor pressure, p.s.i.a. @ 300° F.	3.5 max.
Vapor pressure, p.s.i.a. @ 500° F.	50 max.
Specific heat, B.t.u./lb./° F. @ 300° F.	0.6 min.
Distillation, ° F.:	
I. B. P.	375 min.
50% evaporated	420 min.
90% evaporated	500 max.
End point	550 max.
Thermal stability, research coker test, 300° F.-500° F./600° F./5 hrs., filter, ΔP, in. Hg.	5 max.
Preheater deposit rating	2 max.

Broadly speaking, there is a very large and perhaps infinite number of hydrocarbons which can be classed as fuels. That a given mixture of hydrocarbons can be predicted with reasonable certainty to be combustible in air, however, affords no information as to specific properties peculiar to that mixture by reason of which it is especially qualified as a fuel for a certain purpose. Given a list of the specifications which a fuel must have to be suitable for a given purpose, the problem of producing such a fuel is largely an empirical problem, and can be solved only in small part by theoretical predictions. In the present instance, the problem has been to produce a new type of fuel which will empirically meet the listed specifications for supersonic jet fuels.

The process we have discovered and determined whereby such a fuel can be produced is predicated upon the conversion of so-called polymer gasoline, that is, gasoline produced by the polymerization or alkylation of short-chain hydrocarbons, to C₁₂ and higher boiling branched and straight chain monoolefins and paraffins by treatment with sulfuric acid at controlled process conditions, followed by hydrogenation and refining of the acid-treated product to produce substantially pure paraffins and isoparaffins having approximately at least twelve carbon atoms per molecule. It has been found that a fraction of the product of this process which boils in the range from about 375° F. to about 550° F. has a very high heat content per unit weight, of the order of 18,900 B.t.u.'s or more per pound, a high luminometer number, e.g. 100 or more, and, moreover, fulfills all of the other specific requirements established for fuel for supersonic jet aircraft.

Poly gasoline is usually produced by polymerizing propylene and/or butylene in the presence of a phosphoric acid catalyst at elevated temperatures and pressures, to form C₆-C₉ compounds. This process is well known in the petroleum industry and need not be described in detail herein.

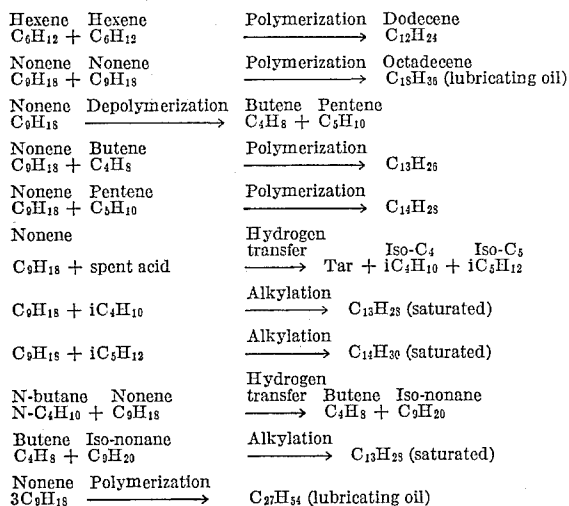
Poly gasoline produced by such a process, or the equivalent thereof, comprises the preferred starting material for the practice of the invention. To this material may be added straight chain olefins boiling in the kerosene range

and/or isoparaffins having about four to ten carbon atoms per molecule, as explained in detail hereinafter.

The resultant mixture is admixed with from 0.5 to 10 parts by weight of 50 to 100% strength sulfuric acid per one part by weight of mixture for a contact time of about 0.1 minute to 1 hour. Pressure is preferably maintained during the reaction in the range from about 10 to 200 p.s.i.g., and temperature is held in the range from about 30 to 200° F.

Preferred conditions are an acid to hydrocarbon ratio of about 3:1 to 6:1, an acid strength of about 60 to 90%, a contact time of about 1 to 5 minutes, a pressure in the range of about 30 to 140 p.s.i.g., and a temperature in the range of about 80 to 120° F.

This acid treatment apparently causes a variety of reactions to take place, not all of which are fully understood. Without intending to limiting the invention, it is believed that some or all of the following reactions take place:



At relatively high acid to hydrocarbon ratios, e.g. 5:1, the poly gasoline is converted by the acid treatment to as much as 90% saturates. In general, the reaction products are straight chain paraffins, isoparaffins of relatively low branching, straight chain olefins and slightly branched mono-olefins, having about twelve to thirty carbon atoms per molecule, together with small quantities of other compounds. The resulting mixture is referred to hereinafter as a synthetic or polymer kerosene.

Following the acid treatment, low boiling components of the stock are preferably separated and recycled to the acid treating unit for further processing. A cut of the poly kerosene boiling above about 375° F. is fractionated and hydrogenated. Following this, the hydrogenated product is fractionated to yield a product which boils in the range from about 375° F. to about 550° F.

The invention is predicated in part on a series of refining operations to which the hydrogenated product is subjected, which have been found to improve the product so that it will meet and even exceed the previously set forth specifications. In accordance with these operations, the fuel is treated with caustic, then with rock salt, and finally is contacted with cold clay. The caustic treatment decreases the high temperature corrosiveness of the fuel and improves its research coker rating. The rock salt filter removes residual alkalinity and water resulting from the flake caustic treatment. The cold clay filter further improves the research coker rating. The final product displays properties which have heretofore been unattainable, and meets the listed specifications for a supersonic jet fuel.

Higher boiling fractions of the hydrogenated product are valuable by-products of the process. A 500–600° F. fraction, for example, is of value as a source of specialty solvents, and a 600–900° F. fraction comprises a high

quality synthetic grease or lubricant blending component which, being of the same chemical origin as the fuel itself, is compatible with the fuel.

The drawing is a diagrammatic flow sheet of a preferred process for producing fuel in accordance with the invention.

Example

Polymer gasoline produced by conventional techniques is introduced through line 10 to a splitter or fractionator 11 in which it is separated into at least a light fraction having an end boiling point of about 375° F., and a higher boiling fraction. The lower boiling fraction is taken from the fractionator 11 through a line 12 to a line 13, in which it is mixed with straight chain olefins boiling in the kerosene range from an outside source which are delivered through a line 14, and recycle C_4 – C_{10} isoparaffins which are delivered through a line 15. The straight chain olefins may be produced, for example, by the thermal and/or catalytic cracking of paraffin waxes. The recycle isoparaffins in line 15 are produced by a later step in the process as will be described hereinafter.

The addition of straight chain olefins to the stock before hydrogenation increases the straight chain paraffin content of the finished fuel, which in turn increases its luminometer number, but also raises its freezing point. The addition of isoparaffins to the fuel lowers its luminometer number, but favorably lowers its freezing point and viscosity at low temperatures. In practice it has been found that the final product must be a mixture of both normal and isoparaffins in order to meet all of the listed specifications. Therefore, the addition of straight chain olefins to line 13 is dependent on the nature of the input gasoline stock and the reaction products produced by the acid treatment at actual process conditions, so that the final blend will meet specifications.

The mixed hydrocarbons in line 13 are passed through a cooler 16 wherein they are cooled to a temperature in the range of about 30 to 200° F., and are then delivered to an acid mixer 17 for treatment with sulfuric acid.

In mixer 17 the hydrocarbons are preferably mixed with 60 to 90% strength sulfuric acid at an operating temperature of about 80 to 120° F., a pressure of about 30 to 140 p.s.i.g., at an acid to hydrocarbon ratio of about 3.0 to 6.0. The hydrocarbons and the acid are contacted for a period of about 0.1 to 5 minutes.

We have found that the sulfuric acid used in this step may be spent alkylation acid of the type, for example, which is produced as a waste in the alkylation of butylene. Normally, spent alkylation acid is of little value to the refiner, who must sell it at a low price for reprocessing; its suitability for use in the acid treating step of the present invention imparts highly favorable economics to this step of the operation.

As previously mentioned, at acid to hydrocarbon ratios of about 5 to 1 or higher, the acid treatment yields high percentages, 90% or more, of saturated products. This is highly desirable since the acid treated product is then more readily hydrogenated to substantial saturation, thereby making possible the use of a hydrogenation catalyst of relatively low activity, as is explained subsequently.

From the mixer 17 the acid and hydrocarbon mixture is sent to a conventional disengager 18 in which the acid is separated from the hydrocarbons which are then sent through a line 21 to a conventional settler 22. Acid separated in the disengager is recycled to line 13 through a line 23. Make-up acid, which may be spent alkylation acid, is added to line 13 as necessary through a line 24, and may constitute 5–10% of the total acid circulating in the system. Spent acid of 50–80% strength containing light tars is separated from the hydrocarbons in settler 22, and is taken off through a line 25 for regeneration.

The acid-treated product is caustic neutralized in a unit 26 to remove entrained free acid, sulfur dioxide, esters, sulfonates, and other acidic compounds. This step may be in accordance with conventional practice. Following

this step the poly kerosene is dried in a conventional rock salt drier 27 to remove entrained water droplets.

Neutral esters and some sulfonates are oil soluble and will pass through the caustic neutralizer 26. These impurities are removed as hydrogen sulfide by subjecting the stock to mild desulfurization in a desulfonator and hydrogen sulfide stripper 28. In this step, the poly kerosene is mixed with hydrogen, which may be reformer hydrogen supplied through a line 29, is heated to a temperature of about 250–400° F., and is contacted with a cobalt-molybdenum catalyst in unit 28 in accordance with conventional desulfonation procedure. H₂S and hydrogen are removed in a reboiler or stripper.

Although a conventional water washing can be employed after the caustic treatment if desired, the desulfonation step has been found to render this unnecessary, thereby obviating the emulsion problems normally attendant water washing.

The neutralized and desulfurized product is then returned to fractionator 11 through lines 31 and 10 to prepare the hydrogenation feed. The fractionator separates lighter compounds boiling up to about 375° F., including unreacted poly gasoline components, which are taken off through line 12, from heavier poly kerosene and/or alkylate which boils above about 375° F., which is taken off through a line 32. The poly gasoline may be recycled to extinction.

Poly kerosene in line 32 is sent through a preheater 33, a heater 34, and is subjected to hydrogenation in a unit 35 with hydrogen from a line 36, whereby unsaturated products are substantially completely saturated. While the hydrogenation step may be conventional and can be effected with any good olefinic hydrogenation catalyst, a preferred technique comprises contacting the polymer kerosene in the presence of hydrogen with regenerated spent cobalt molybdenum catalyst. Such catalyst is commonly utilized for naphtha desulfurization in catalytic reforming operations and is generally available in refineries at relatively low cost. We have found that because of the high proportion of saturates in the hydrogenation feed, as previously mentioned, the hydrogen requirements of the stock are such that this low cost catalyst is adequate, and its use provides another substantial economic advantage. A quench stream 37 is taken off from line 32 and is injected into the hydrogenator between the respective beds thereof to prevent the temperature from becoming too high during the exothermic reaction.

Straight chain olefins in the kerosene boiling range can be charged directly to the hydrogenating unit 35 through lines 14 and 32 to increase the proportion of normal paraffins in the final product as desired. As previously explained, straight chain paraffins are useful for blending with lower freezing isoparaffins produced in accordance with the process, so that the final product will have a freezing point and luminometer number both of which will meet specifications.

From the hydrogenation unit 35 the saturated product is delivered through a line 37 to the cooling section of heat exchanger 33, to a cooler 38 and then to a disengager 39 in which entrained hydrogen and other light gases are separated and returned to line 32 through recycle hydrogen line 40. Following this step the product is sent to a vacuum fractionation unit 42 through a line 41 wherein the various product cuts are separated. Depending upon specific products desired, the hydrogenated poly kerosene may be separated into several fractions, separation into four fractions as follows being illustrated in the diagram:

- (1) Light C₄–C₁₀ isoparaffins are taken off as overhead through line 15 and are recycled to line 13 in which they are mixed with poly gasoline for further reaction in the acid treating unit 17.
- (2) Supersonic jet fuel boiling in the range of about 375° F. to about 550° F. is taken off through line 43 for final treatment.
- (3) Specialty solvents boiling in the range of about 500 to 650° F. are taken off through line 44.

- (4) A high boiling 600 to 900° F. product which comprises substantially pure C₁₇–C₃₀ normal and isoparaffins is taken off through line 45. This fraction may be processed into saturated products for transformer oils. Since jet engine lubricating oils produced by the process of this invention are compatible with jet engine fuels produced by the same process, they can be admixed with the fuel to eliminate the necessity for a separate lubricating system in the engine.

The fuel cut taken off through line 43 is given a final treatment which has been found to markedly improve its ultimate properties. The fuel is first treated in a flake caustic unit 46, and is then sent to a rock salt treating unit 47 in which residual alkalinity and water are removed. Finally the fuel is treated with cold clay, e.g. bauxite, in unit 48. These final treatments have been found effective to reduce the high temperature corrosiveness of the fuel and to improve the research coker test rating of the fuel by removing small traces of undesirable compounds including mono- and di-olefins and organo-metallics.

Specifications of a typical supersonic jet fuel produced in accordance with the process of this invention are as follows.

Net heating value, B.t.u./lb.	18,925
Freezing point, ° F.	—85
Luminometer number	100
Viscosity, cs. @ —30° F.	10
Vapor pressure, p.s.i.a. @ 300° F.	3.2
Vapor pressure, p.s.i.a. @ 500° F.	47
Specific heat, B.t.u./lb./° F. @ 300° F.	0.615
Distillation. ° F.:	
I.B.P.	378
50% evaporated	422
90% evaporated	440
End point	485
Thermal stability, research coker test, 300° F.—500° F./600° F./5 hrs., filter, ΔP, in. Hg.	0.5
Preheater deposit rating	#1

It will be seen that this fuel meets all of the specifications listed previously for a supersonic jet fuel.

What is claimed is:

1. A process for producing a supersonic jet fuel which comprises: treating a hydrocarbon feedstock consisting essentially of aliphatic hydrocarbons in the range of C₆–C₉ with 50–100% H₂SO₄ in an H₂SO₄/feedstock ratio of 0.5–10/1 by weight at a temperature and pressure of about 30–200° F. and 10–200 p.s.i.g. respectively for a period of about 0.1–60 minutes whereby at least a portion of said aliphatic hydrocarbons is polymerized and alkylated to form a hydrocarbon mixture comprising saturated and unsaturated aliphatic hydrocarbons in the C₁₂–C₃₀ range; subjecting at least a portion of said hydrocarbon mixture to hydrogenation to convert said unsaturated aliphatic hydrocarbons to saturated aliphatic hydrocarbons; and fractionating the resultant hydrogenated mixture to yield a fraction consisting essentially of saturated aliphatic hydrocarbons having a boiling range of about 375–550° F., a heating value above about 18,900 B.t.u./lb., a freezing point no higher than about —30° F., a luminometer number of at least about 100, a viscosity no greater than about 15 cs. at —30° F., a vapor pressure no higher than about 50 p.s.i.a. at 500° F., a research coker filter pressure drop no greater than about 5 in. Hg and a research coker preheat deposit rating no greater than about 2.

2. A process according to claim 1 in which the H₂SO₄ is 60–90% H₂SO₄, the H₂SO₄/feedstock ratio is about 3–6/1 the temperature and pressure are about 80–120° F. and 30–140 p.s.i.g., respectively, and the treatment period is about 1–5 minutes.

3. A process according to claim 1 in which said hydrocarbon mixture is neutralized, desulfurized and then fractionated to separate a fraction boiling below about

375° F., the higher boiling fraction then being subjected to hydrogenation and fractionation.

4. A process according to claim 1 in which straight chain olefins in the kerosene boiling range are added to the hydrocarbon mixture prior to hydrogenation.

5. A process for producing a supersonic jet fuel which comprises: treating a hydrocarbon feedstock consisting essentially of aliphatic hydrocarbons in the range of C₆-C₉ with 60-90% H₂SO₄ in an H₂SO₄/feedstock ratio of 3-6/1 by weight at a temperature and pressure of about 80-120° F. and 30-140 p.s.i.g., respectively, for a period of about 1-5 minutes, whereby at least a portion of said aliphatic hydrocarbons is polymerized and alkylated to form a hydrocarbon mixture comprising saturated and unsaturated aliphatic hydrocarbons in the C₁₂-C₃₀ range; neutralizing and desulfurizing said hydrocarbon mixture; fractionating said neutralized and desulfurized hydrocarbon mixture to separate a fraction boiling below about 375° F.; adding straight chain olefins in the boiling range of kerosene to the higher boiling fraction and hydrogenating the resultant mixture to convert the unsaturated aliphatic hydrocarbon content thereof to saturated aliphatic hydrocarbons; fractionating the hydrogenated product to yield a fraction consisting essentially of saturated aliphatic hydrocarbons having a boiling range of about

375-550° F., a heating value above about 18,900 B.t.u./lb., a freezing point no higher than about -30° F., a luminometer number of at least about 100, a viscosity no greater than about 15 cs. at -30° F., a vapor pressure no higher than about 50 p.s.i.a. at 500° F., a research coker filter pressure drop no greater than about 5 in. Hg, and a research coker preheat deposit rating no greater than about 2, and refining said fraction by treating it with flake caustic, rock salt and cold clay.

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