United States Patent Office 3,112,799 Patented Dec. 3, 1963

3,112,799

CORING FLUID

Julius P. Gallus, Tulsa, Okla., assignor to Jersey Production Research Company, a corporation of Delaware

No Drawing. Filed Mar. 9, 1960, Ser. No. 13,695
8 Claims. (Cl. 175—58)

The present invention relates to compositions useful in drilling oil wells, gas wells and similar boreholes in the earth and more particularly relates to a fluid for use in the core drilling of such boreholes. In still greater particularity, the invention relates to an improved coring fluid containing a latex which is unstable in the presence of polyvalent cations found in subsurface strata and a minor amount of a resin possessing an affinity for surfaces within such strata.

The volumetric oil content of subsurface, oil-bearing reservoirs is normally calculated in terms of the reservoir volume, the formation volume factor, the average reservoir porosity, and the average oil content of the reservoir. In reservoirs wherein a number of development wells have been drilled, the reservoir volume and the formation volume factor can usually be determined with reasonable accuracy by preparing structural maps and by measuring the gravity, temperature, pressure and gas content of the oil under reservoir conditions. The average porosity and average oil content of the reservoir are generally determined by analyzing cores recovered from a number of development wells. Values for volumetric oil content, together with other data, are widely used to forecast the productive life of oil and gas reservoirs, to select the primary recovery techniques most suitable for particular reservoirs, and to assess the susceptibility of such reservoirs to later secondary and tertiary recovery processes. Experience has demonstrated, however, that volumetric oil content determined in this manner is frequently not an accurate indication of the actual quantity of oil present in a reservoir. Some reservoirs continue to produce long after they should have been exhausted of oil; while others are depleted much earlier than would be expected on the basis of the calculated volumetric oil content. Studies have shown that these discrepancies are primarily due to errors in average oil content as determined by core analysis.

Conventional core drilling systems utilize an annular bit and core barrel which are rotated from the earth's surface by means of a rotary drill string. A coring fluid is circulated downwardly through passages in the drill string, barrel and bit in order to maintain pressure on the formation and thus prevent the escape of fluids contained therein. Cuttings produced by the bit are entrained in the coring fluid and returned to the surface through the annulus surrounding the drill string. As the bit cuts away the formation, the central core which remains is encased in the barrel. The core barrel is generally provided with means for breaking off the core after the barrel has been filled and with closures which protect the core against contamination by fluids present in the borehole. Pressure core barrels which can be sealed against changes in pressure are also used. After the core has been cut, the drill string is withdrawn from the borehole and the core is recovered.

Studies have shown that the pressure maintained at the bottom of the borehole during a coring operation has a profound effect upon the fluids in cores subsequently recovered. If this pressure is less than the formation pressure, fluids contained in the formation will tend to flow out of the core into the borehole until equilibrium is established. If, on the other hand, the bottom-hole pressure exceeds the formation pressure, the coring fluid will tend to flow into the interstices of the formation

and displace any oil, gas or water contained therein. In either case, the result is a change in the fluids content of the core such that subsequent measurement of the amount of fluids present will not accurately reflect the original fluids content of the cored formation. Since this change in fluids content occurs continuously as the core is cut, the use of a pressure corebarrel does not prevent it.

Several methods for avoiding the difficulty outlined above have been proposed in the past. The most obvious of these involves carrying out the coring operation without any pressure differential between the coring fluid and the formation. This is impractical because the formation pressure cannot be conveniently measured during core drilling and, even if it could, because the fluid pressure cannot be controlled with sufficient accuracy. The use of coring fluids which will not invade the formation under pressures well in excess of the formation pressure has been suggested but efforts to develop a satisfactory fluid have been unsuccessful. Mercury, plastics, molten metals and other materials advocated in the past all invade the formation to an appreciable extent and hence lead to changes in fluids content. In addition, the materials proposed for this purpose have generally been costly and difficult to use and in many cases require highly specialized core bits and core barrels. Other systems, including the use of tracers which permit determination of the extent to which core invasion has occurred and systems for freezing the core, have been proposed but have not been found generally effective.

The present invention provides a new and improved coring fluid which obviates the difficulties outlined above and permits the recovery of core samples having fluids contents truly representative of those of the formations from which the cores are taken. In accordance with the invention, it has now been found that certain polymeric latices modified by the addition thereto of minor amounts of certain resins will instantly solidify upon contact with subsurface strata to form a tough, impermeable film. The use of such modified latices as coring fluids permits the surfaces of cores to be sealed as they are cut, thus entrapping fluids originally present in the cored formation and preventing their escape. The rapidity with which the film is formed is such that essentially none of the coring fluid has an opportunity to invade the core and hence displacement of connate fluids within the core does not occur. On recovery of the sealed cores, the film can readily be peeled from the core surface without damage to the surface. Core permeability and porosity are substantially unaffected by the fluid.

The modified latices of the invention have numerous applications in addition to being useful as coring fluids. They may be employed as lost circulation agents for sealing the walls of boreholes in order to permit subsequent loss of the drilling fluid to porous strata. They may be used to coat subsurface strata in order to prevent their breakdown due to hydration. They may be employed prior to well cementing operations as a means for preventing the cement from penetrating into porous zones. They are useful as fracturing fluids in operations where low fluid losses and non-permanent plugging are desired. They may be used to line mud pits, storage caverns and similar cavities in order to improve their ability to retain fluids. They may be used as water-shut-off agents during air drilling operations. These and other uses for the modified latices will be apparent to those skilled in the art after reading the following disclosure.

The polymeric latices which form the major component of the modified latices employed in accordance with the invention are emulsions of oil-resistant elastomers which readily coagulate in the presence of polyvalent

cations to form films which are impervious to oil, gas, water and other fluids. Suitable latices may be derived from natural rubber or from synthetic elastomers prepared by the polymerization of unsaturated monomers. Studies have indicated that the chemical compositions of the elastomers contained in the latices generally have little effect on their suitability for purposes of the invention and that latices containing a wide variety of synthetic elastomers may be successfully employed.

Latices suitable for purposes of the invention may be derived from synthetic elastomers prepared by the polymerization of olefinically-unsaturated hydrocarbons or by the copolymerization of such hydrocarbons with other olefinically-unsaturated monomers. The olefinically-unsaturated hydrocarbons utilized may be olefins such as isobutylene and the pentylene; diolefins such as butadiene, isoprene, piperylene, dimethyl butadiene and 2-methyl pentadiene; or vinyl aromatics such as styrene, methyl styrene and vinyl toluene. Mixtures of such hydrocarbons may also be used. Olefinically unsaturated monomers which may be copolymerized with the hydrocarbons include halogenated olefinically-unsaturated compounds such as vinyl chloride, allyl chloride and chloroprene; unsaturated esters such as vinyl acetate, allyl propionate, methyl methacrylate, ethyl acrylate, methyl fumarate, ethyl maleate and propyl itaconate; unsaturated nitriles such as acrylonitrile, methacrylonitrile, ethyl acrylonitrile and chloroacrylonitrile; unsaturated ketones such as methyl vinyl ketone; cyclic vinyl compounds such as vinyl pyridine; and mixtures thereof. It will be recognized that all of these elastomers are not equally effective for purposes of the invention.

Specific examples of elastomers prepared from the foregoing monomers which are suitable in the form of latices for purposes of the invention include polyisobuytlene, polystyrene, polybutadiene, polyisoprene, butadiene-isoprene copolymers, isoprene-isobutylene copolymers, isobutylene-styrene copolymers, piperylene-vinyl acetate copolymers, butadiene-styrene-vinyl chloride copolymers, butadiene-acrylonitrile copolymers, butadiene-methacrylonitrile copolymers, and isoprene-chloroprene vinyl acetate copolymers.

Latices containing the foregoing elastomers may be prepared by the emulsion polymerization of suitable monomers or by the emulsification of organic solutions of dry elastomers with water or other liquid, followed by removal of the solvent. The method utilized will depend primarily upon the elastomer used. Many conjugated diolefin polymers and copolymers of conjugated diolefins with monomers containing a vinylidene linkage, polybutadiene and copolymers of 1-3-butadiene with styrene, acrylonitrile or vinyl chloride for example, can readily be prepared by emulsion polymerization and recovered in latex form. Other elastomers, styrene-isobutylene and isobutylene-isoprene copolymers for example, are best prepared by bulk or solution polymerization processes which do not result in the formation of latices. Elastomers prepared in the latter manner must subsequently be emulsified with the aid of a solvent to produce latices. Processes for preparing latices by both methods are widely described in the chemical and patent literature. A typical emulsion polymerization process is described in U.S. Patent 2,460,038, issued to George E. Serniuck on January 25, 1949. A description of one method for preparing latices from dry elastomers ultilizing an organic solvent may be found in U.S. Patent 2,799,662, issued to John L. Ernst et al. on July 16, 1957.

Latices consisting of aqueous emulsions of suitable elastomers are normally employed in the practice of the invention but in some cases emulsions in which the continuous phase is a liquid other than water may be preferred. One instance of this occurs in coring operations carried out in very high temperature strata where a liquid having a boiling point above that of water must be used. Another instance occurs in the case of arctic operations where an aqueous emulsion would quickly freeze during storage. Any of a number of chemically non-reactive liquids which have the proper temperature characteristics and do not act as solvents for the elastomers employed may be utilized. Normal decane, for example, will be suitable for use with certain elastomers.

The latices employed in accordance with the invention are preferably homopolymers prepared by the emulsion polymerization of conjugated diolefins containing from about 4 to about 6 carbon atoms per molecule or copolymers prepared by the copolymerization of such a diolefin with one or more olefinically-unsaturated monomers containing from about 4 to about 8 carbon atoms per molecule. Preferred latices include polybutadiene, polyisoprene, butadiene-styrene copolymer, butadiene-acrylonitrile copolymer, butadiene-methacrylonitrile copolymer, butadiene-vinyl acetate copolymer and butadiene-isoprene copolymer latices. Butadiene-acrylonitrile copolymer latices are particularly preferred.

The latices useful for purposes of the invention are characterized by the fact that they are rapidly coagulated upon contact with calcium, magnesium and other polyvalent cations found in subterranean formations. They thus differ from latices employed in the past as additives for improving the viscosity, gel strength and fluid loss characteristics of drilling muds. Conventional drilling muds generally contain clays, barytes, gypsum, lime and similar materials in relatively high concentrations and hence are rich in polyvalent cations. Latices used as additives in such drilling muds must therefore be highly stable in the presence of polyvalent cations in order to avoid coagulation and loss of the improved properties which they are intended to confer. Such latices are generally stabilized by the addition of stabilizing agents after they are formed. They do not coagulate during use. The invention does not contemplate the use of stable latices as additives to fluids containing polyvalent cations and instead is predicated on the use of unstable latices substantially unadulterated by the presence of materials conventionally employed as stabilizing agents. These unstable latices do not come in contact with appreciable quantities of polyvalent cations until they contact the subsurface strata. Polyvalent cations are always present on surfaces of such strata, although sometimes in low concentrations, and hence the latices coagulate on contact with the strata to form impermeable films. The extremely rapid film formation which occurs restricts the coagulation to that part of the latex in contact with the strata and prevents the entire latex stream from setting up as a solid.

Although the latices employed in accordance with the invention are relatively unstable and quickly coagulate in the presence of polyvalent cations in very low concentrations, they should nevertheless have sufficient shear stability to permit them to be pumped without fear of coagulation. This requires that the stability characteristics of the latices be carefully controlled. Latex stability depends upon a number of factors, including the amount of emulsifier, dispersing agent or stabilizer used in preparing the latex, the pH of the latex product, and the particle size of the dispersed elastomer in the latex. All of these factors are somewhat interrelated and may be varied widely depending upon the particular emulsifier used, the elastomer employed, and the conditions under which the latex is prepared. It is therefore impractical to attempt to prescribe the exact physical properties which characterize latices suitable for the invention. The applicability of any particular latex can readily be determined, however, by simply contacting it with a surface coated with a very weak solution of polyvalent cations and by circulating it through a laboratory pump to stimulate the shear stresses encountered in a well circulation system, observing in each case whether coagulation of the latex occurs.

In most cases it is preferred that the latices employed in accordance with the invention have pH values between about 8.5 and about 10, although as pointed out above latices of equal stability prepared with different elastomers and different emulsifiers may vary in pH over a considerable range. Studies have indicated that many latices having pH values below about 8.5 have insufficient shear stability to permit their circulation through pumps and that those whose pH exceeds about 10 are generally too stable to coagulate readily in the presence of very dilute polyvalent cation solutions. Typical latices suitable for purposes of the invention have average elastomer particles ranging between about 0.05 and about 2.0 microns in diameter. Latices having average particle sizes outside this range may in some case be used, since the use of a highly efficient emulsifier during preparation of the latex may result in a latex of the proper stability containing considerably larger particles; while on the other hand a poor emulsifier may necessitate the use of smaller elastomer particles. The 0.05 to 2.0 microns range is, however, generally to be preferred.

Laboratory studies have shown that the solids contents of the latices useful for purposes of the invention are not highly critical but that dilution with water tends to decrease latex shear stability and increase latex resistance to coagulation in the presence of polyvalent cations. In some cases this provides a convenient means for controlling the stability properties of the latices employed. Latices containing from about 5 to about 70% solids are generally suitable for purposes of the invention, those containing from about 20 to about 50 weight percent solids being preferred.

The resins employed as the second component of the improved coring fluids of the invention are high molecular weight water-soluble or water-dispersable, oil-insoluble, polymeric materials which are readily adsorbed upon subsurface strata. A variety of such materials have been used in drilling muds and similar compositions in order to improve their stability, water-loss characteristics, and similar properties. It does not appear that chemical composition of the materials utilized is highly critical. Suitable materials include such diverse substances as alginic acid, sodium salts of alginic acid, sodium carboxymethyl cellulose, sodium carboxyethyl cellulose, polymeric alcohols such as polyvinyl alcohol, hydrolyzed or partially hydrolyzed polyacrylamides and starch. Other resinous materials possessing the requisite stability and adsorption properties will suggest themselves to those skilled in the art.

In general the resins employed in the coring fluids should have molecular weights in excess of about 50,000 as determined by the Staudinger method. Lower molecular weight resins normally are of such small particle size that they can freely enter the pores of the subsurface strata. The precise molecular weight required for best results depends in part upon the particular resin utilized but molecular weights between about 500,000 and about 2,000,000 are generally preferred.

It has been found that only very small quantities of the resins need to be added to the latices in preparing the improved coring fluids of the invention and that the use of too much resin impairs the effectiveness of the coring fluid. The amount required depends to some extent upon factors such as the molecular weight of the resin, the stability characteristics of the latex, and the solids content of the latex. In general, however, from about 0.005 to about 2.0 weight percent of resin will be employed. From about 0.05 to about 1.0 weight percent is preferred.

In preparing the coring fluids, the finely divided resin may be simply added to the latex and dissolved or dispersed therein by agitation. The shear stability characteristics of the latices employed prevent coagulation during the agitation step.

Core drilling operations utilizing the improved coring fluid of the invention may be carried out with conventional apparatus familiar to those skilled in the art. A variety of commercially available core bits and core barrels may be used. The coring fluid may be circulated down the drill string through channels in the barrel and bit so that it emerges adjacent the cutting surfaces of the bit. The fluid contacts the core surfaces as the surrounding rock is cut away and continuously forms a film on the surfaces which is impermeable to oil, gas and water. The essentially instantaneous formation of the film precludes invasion of the core. The coated core is encased in the core barrel. After a core of sufficient length has been cut, the barrel is withdrawn to the surface and the core is recovered. The film on the core surface can readily be peeled off to expose the core sample.

The nature and objects of the invention can be more fully understood by referring to the results of experimental work carried out to test and demonstrate the use of the improved coring fluid.

In a first series of tests, a number of cores were cut from blocks of porous sandstone using apparatus closely resembling that employed in field core drilling operations and a conventional bentonite drilling mud. The rock samples utilized measured 12 inches square by 24 inches high and were prepared for the test by displacing the fluids contained therein and replacing them with measured amounts of oil and brine. Each block of sandstone was first completely dehydrated, hermetically sealed, and thereafter subjected to a high vacuum. A synthetic brine closely resembling a typical formation water was forced into the sealed and evacuated block. Oil was then forced into the block under pressure. The volumes of brine and oil injected and the volume of brine displaced by the oil were precisely measured. A typical block contained 65 percent oil and 35 percent brine. The oil employed was a 12 centipoise white oil. The brine used contained 2,500 parts per million of calcium chloride, 1,000 parts per million of magnesium chloride, and 26,000 parts per million of sodium chloride and thus had a polyvalent cations content typical of oil field brines.

Cores measuring about 17 inches in length and 2½ inches in diameter were cut from the blocks prepared in the manner described above. A 6½ inch outer diameter core bit and a core barrel of conventional design attached to a length of drill pipe so that the pipe core barrel and bit could be rotated were employed. The block of sandstone to be cored, the core bit, and the core barrel were encased in a pressure-tight chamber in order to permit the simultation of high formation pressure. Bentonite drilling mud was circulated through the drill pipe, core barrel and core bit from a mud reservoir by means of a high pressure pump. Drilling mud containing cuttings was withdrawn through the annulus surrounding the drill string, cuttings were removed and the drilling mud was returned to the reservoir. Facilities for measuring the fluids contents of cores recovered from the core barrel were provided. The drilling mud was circulated under pressure differentials which ranged from about 40 to about 100 pounds per square inch in excess of the pressure within the sandstone block. The mud circulation rate was about 97 gallons per minute. This particular method and apparatus were selected because earlier tests had shown that the results obtained were comparable to those obtained in actual field tests.

Analysis of a series of cores cut with bentonite drilling mud in the manner described above showed that the mud had invaded the cores and largely displaced the oil and water originally present therein. Displacement of 10 volume percent of the connate fluids from a core is considered to be the maximum displacement that can be tolerated if analysis of the fluids recovered from cores is to be significant. Screening tests showed that considerably more than 20 volume percent of the fluids originally present had been displaced by the bentonite mud in every case and therefore further measurement of the displacement were not made. The results thus obtained are

typical of oil field core drilling operations, where the displacement of 50 volume percent or more of the oil and water contained in the cored strata is not uncommon.

Following the tests using bentonite drilling mud as the coring fluid in the manner described above, tests were made using the improved coring fluid of the invention. The latex employed in the coring fluid was one prepared by the emulsion polymerization of 65 weight percent butadiene and 35 weight percent acrylonitrile in the presence of a persulfate catalyst and about 8 weight percent of a potassium rosin soap emulsifier. The latex contained about 0.8 weight percent of an anti-oxidant but had not been chemically stabilized after its formation. It had a 40 weight percent solids content, an average elastomer particle size of 0.07 micron, and a pH of about 9.5. The surface tension was 50 dynes per centimeter at 25° C. To this latex was added 0.07 weight percent of a partially hydrolized polyacrylamide. The polyacrylamide hydrolyte had an average molecular weight of about 1,500,000 Staudinger. The apparatus employed, the sandstone used and the method for preparing the sandstone were identical to those in the earlier tests. The results obtained upon analysis of the recovered cores are shown in the following table.

Core	Coring Fluid Circulation Rate g.p.m.	Coring Fluid Pressure Differential, p.s.i.	Coring Fluid Invasion, Percent of Core Vol.
A	13	25	1.9
B	13	50	0
C	15	100	0.15
D	97	100	0

It can be seen from the foregoing table that the coring fluid of the invention permitted the recovery of cores from which only very small amounts of the fluids originally present in the cored formation had been displaced. At differential pressures of 50 pounds per square inch or higher, the displacement was insignificant. Each recovered core was encased in a thin, flexible seal which was easily removed. Tests showed that the permeability and porosity of the sandstone to water were unaffected by the formation and subsequent removal of the film. The coring fluid exhibited no tendency to coagulate prematurely during the tests.

Similar tests of a latex not containing the resin component of the coring fluids of the invention showed that the latex alone invaded the core and displaced about 5 percent of the connate fluids originally present therein. The unstable latices utilized in accordance with the invention are by themselves greatly superior to conventional drilling muds for coring purposes but do not possess the extremely rapid film-forming characteristics which distinguish the coring fluids of this invention. The use of both the latex and a small amount of resin are essential if cores containing substantially all of the connate fluids originally present are to be recovered.

A still further test was carried out to determine whether the unstable latex containing 0.07 wt. percent of partially hydrolized polyacrylamide as described above could be successfully used in full scale oil field pumping and drilling equipment. The test was carried out with a Mayhew drilling rig, a conventional core barrel, and 7½ inch outer diameter core bits of both the drag bit and the diamond bit types. During the drilling operation, the weight on the bit ranged between 5,000 and 7,000 pounds, the coring fluid circulation rate was varied between about 75 and about 120 gallons per minute, and the bit rotational speed ranged between about 30 and about 45 revolutions per minute.

A total of 25 feet of core was cut from shale and sandstone during the test. Core recovery was 100%. All of the core was sealed in a fluid impermeable film essentially identical to that obtained in the earlier tests.

The fluid carried bit cuttings to the surface satisfactorily and no difficulties due to premature coagulation were encountered. It was found that centrifugal forces up to 400 G's in the centrifugal fluids-solids separator used intermittently to remove the cuttings from the fluid did not adversely affect the fluid. The type of bit employed apparently had no effect upon film formation. Neoprene rubber pump and tool parts were unaffected by the fluid, although it was found that oil-sensitive rubber parts of the equipment not made of neoprene were attacked by the fluid to some extent. Circulation of the fluid past a cemented section of the borehole caused no difficulties.

The results of the above tests clearly demonstrate that the coring fluid of the invention can be used to recover cores during full scale core drilling operations. Use of the fluid permits the recovery of cores which are more representative of subsurface conditions than cores recovered in the past, both from a quantitative and a qualitative standpoint.

What is claimed is:

1. In a process wherein a rock core is cut from a subterranean formation on which polyvalent ions are present by means of a core bit and is thereafter encased in a core barrel, the improvement which comprises contacting said core as the core surfaces are exposed by said bit with a shear-stable latex containing an oil-resistant film-forming elastomer coagulable in the presence of polyvalent ions and from about 0.005 to about 2.0 wt. percent, based upon said latex, of an oil-insoluble, water-dispersible polymer readily adsorbed on subsurface strata, said polymer having a molecular weight in excess of about 50,000 Staudinger.

2. A process for the recovery of a rock core from a subterranean formation on which polyvatent ions are present which comprises cutting said core with an annular bit; contacting the formation beneath said bit as the core surfaces are exposed with a shear-stable aqueous emulsion containing a copolymer of a conjugated diolefin containing from about 4 to about 6 carbon atoms per molecule and an olefinically-unsaturated monomer containing from about 4 to about 8 carbon atoms per molecule, said emulsion being unstable in the presence of polyvalent ions and containing from about 0.005 to about 2.0 weight percent, based upon the emulsion, of an oil-insoluble, water-dispersible polymer readily adsorbed upon subsurface strata, said polymer having a molecular weight in excess of about 50,000 Staudinger; and thereafter encasing said core in a core barrel.

3. A process as defined by claim 2 wherein said copolymer is a butadiene-acrylonitrile copolymer.

4. A process as defined by claim 2 wherein said polymer is a polyacrylamide.

5. A process as defined by claim 2 wherein said polymer is a carboxymethylcellulose.

6. A core drilling process which comprises cutting a core from a subterranean formation on which polyvalent ions are present with an annular drill bit, continuously contacting said formation beneath said bit with a latex containing an oil-resistant elastomer coagulable by polyvalent ions and a minor amount of an oil-insoluble, water-dispersible polyacrylamide having a molecular weight in excess of about 50,000 Staudinger to form a fluid impervious film on said core as the core surfaces are exposed by said bit, and thereafter encasing said core covered by said film in a core barrel.

7. A core drilling process which comprises cutting a core from a subterranean formation on which polyvalent ions are present with an annular drill bit, continuously contacting said formation beneath said bit with a latex containing an oil-resistant elastomer coagulable by polyvalent ions and a minor amount of an oil-insoluble, water-dispersible polymeric alcohol having a molecular weight in excess of about 50,000 Staudinger to form a fluid impervious film on said core as the core surfaces

are exposed by said bit, and thereafter encasing said core covered by said film in a core barrel.

8. A core drilling process which comprises cutting a core from a subterranean formation on which polyvalent ions are present with an annular drill bit, continuously contacting said formation beneath said bit with a latex containing an oil-resistant elastomer coagulable by polyvalent ions and a minor amount of an oil-insoluble, water-dispersible alginic acid polymer having a molecular weight in excess of about 50,000 Studinger to form a fluid impervious film on said core as the core surfaces are exposed by said bit, and thereafter encasing said core covered by said film in a core barrel.

References Cited in the file of this patent

UNITED STATES PATENTS

2,121,036	Irons	June 21, 1938
2,425,768	Wagner	Aug. 19, 1947
2,473,929	Wilson	June 21, 1949
2,718,497	Oldham et al.	Sept. 20, 1955
2,775,557	Morgan	Dec. 25, 1956
2,805,990	Bergman	Sept. 10, 1957
2,880,969	Williams	Apr. 7, 1959
2,914,498	Quarles et al.	Nov. 24, 1959
2,947,146	Loofbourow	Aug. 2, 1960