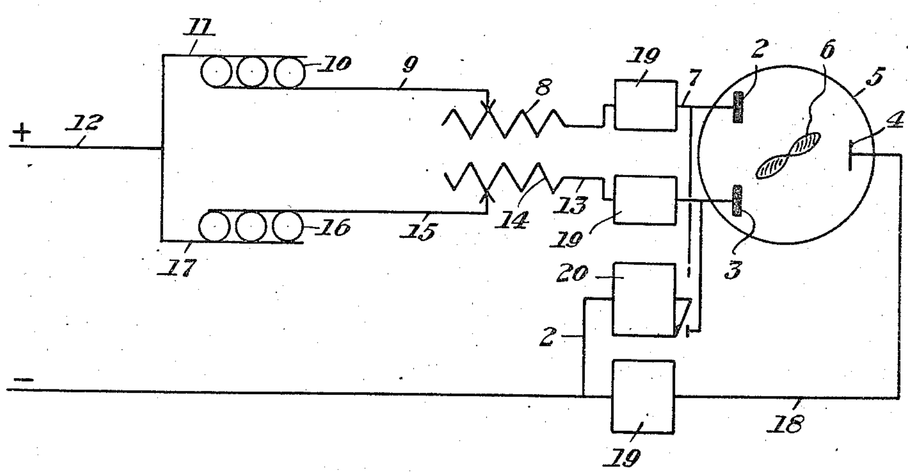
April 16, 1946. W. E. BRADT ET AL 2,398,614

ELECTRO-DEPOSITION OF MANGANESE

Filed March 24, 1938



INVENTORS
Wilber E. Bradt,
Harold H. Oaks,
~~Alfred A. Edwards~~
~~and Luther R. Taylor~~
by
Stebbins, Blenko & Parmelee.
Their Attys.

Patented Apr. 16, 1946 2,398,614

UNITED STATES PATENT OFFICE

2,398,614

ELECTRODEPOSITION OF MANGANESE

Wilber E. Bradt, Orono, Maine, and Harold H. Oaks, Newport, Wash., assignors to Vanadium Corporation of America, New York, N. Y., a corporation of Delaware

Application March 24, 1938, Serial No. 197,850

11 Claims. (Cl. 204—45)

This invention relates to the electrodeposition of metallic manganese from aqueous solutions containing manganese salts. One object of the invention is to provide deposits of metal closely approaching 100 per cent purity. Another object is to produce deposits that are bright and possess metallic luster. Another object is to establish conditions that will permit deposition of the metal from the same solution for long periods of time, thus establishing a basis for continuous extraction of the metal from its ores and the preparation of thick electroplates of the metal. Another object is to make possible the coating of many different metals with manganese metal for protective and decorative purposes and the like. Other objectives will be obvious from the descriptive matter to follow.

During a period of over 75 years, efforts have been made to deposit by means of the application of electric current to aqueous solutions of manganese compounds, appreciable amounts of pure metallic manganese. These have been very notably unsuccessful. In some instances, the deposited substance has been of low purity, in others of loose or spongy or non-coherent structure, in others of scaly or powdery nature. Reference has also been made in the literature to the gray or black appearance of these deposits, even in cases where some semblance of compactness has been reported.

Insofar as we have been able to determine, no electrodeposit of manganese of extremely high purity and considerable thickness has heretofore been obtained that possesses simultaneously silver-white appearance, noncrystallinity to the unaided eye, compactness, smoothness, coherence, is adherent to a metallic cathode such as copper, is resistant to corrosion and is capable of taking a high polish on buffing.

The present invention provides a process whereby manganese may be produced which has all of these desirable properties in marked degree.

The color of the manganese deposit is especially important, not only from the standpoint of appearance but also because it is an indication of the purity of the manganese. The dark color of electrodeposited "manganese" produced by methods described in the prior art and confirmed by us is due to inclusions of manganese dioxide. This was definitely established by carefully dissolving a dark deposit in very dilute cold hydrochloric acid. Manganese dioxide goes into solution readily only in concentrated hydrochloric acid. It was found that such dark or black deposits, upon immersion in dilute acid, remained in relief. Another evidence of the presence of manganese dioxide in these dark or black deposits is the yellow or brown colored solution obtained by dissolving the dark or black deposit in concentrated hydrochloric acid; this color is due to the formation of higher valence chlorides of manganese.

Pure electrodeposited manganese as produced by our process is silver-white in color. Several of these silver-white deposits were disolved in hydrochloric acid and titrated with standard potassium permanganate, according to the Volhard method; the results showed 100 percent purity However, color is considered to afford a more delicate indication than chemical analysis of complete absence of oxides, as with increasing oxide content the color of the deposit is no longer silver-white but ranges through gray to brown to black.

We have carried out a large number of tests employing insoluble (platinum) anodes for depositing manganese from various solutions but have found that the use of insoluble anodes is generally objectionable for several reasons. Any process using an insoluble anode must necessarily be subject to depletion of the manganese ion during electrolysis. This brings about substantial alteration of the composition of the electrolyte and requires the addition of one or more materials for purpose of adjustment. When using manganese chloride, for example, as the electrolyte with platinum anodes, chlorine and oxygen are normally evolved at the anode. At the same time, manganese dioxide is formed at the anode. These objections are preferably overcome or diminished in our process by using a soluble manganese anode or a combination of soluble manganese anodes and insoluble anodes or by the use of certain types of addition agents. The use of a soluble manganese anode enables the application of current densities approximately double those possible when an insoluble anode is employed. For example, the use of a soluble manganese anode makes possible a reduction of approximately 50 per cent in the power consumed at any fixed current density, or total current. Hence with no change in current efficiency, twice as much metal is deposited with a given power input. Further, the use of an insoluble platinum anode, in addition to requiring voltages of 7 to 8, is accompanied by the formation of hydrated manganic oxide. The soluble manganese anode requires approximately 1.5 volts and is accompanied by the formation of hydrated manganous oxide. This, moreover, can be prevented or decreased by the addition to the manganese chloride solution of certain ammonium salts—for example, ammonium chloride. Ammonium chloride is preferably employed in the amount of about 30 grams per liter, but this may be varied according to conditions from about 10 grams per liter to saturation. The following table gives the results of tests employing a soluble manganese anode of 96% manganese purity, the electrolyte containing manganese chloride and ammonium chloride in the proportions given.

Table

	A	B	C
Anode	Platinum	Platinum	96% Mn.
Electrolyte (gm. per liter)	712 $MnCl_2.4H_2O$	700 $MnCl_2.4H_2O$, 30 NH_4Cl	700 $MnCl_2.4H_2O$, 30 NH_4Cl.
Voltage	Varies 9.0 to 16.0	Not recorded	4.9.
Cathodic current density, amp./sq. dm.	20.0	20.0	20.0.
Condition of electrolyte	Brown hydrated manganic oxides formed at anode as soon as electrolysis began and increased in amount as the run proceeded.	Clear for 5 min. followed by formation of manganic oxides.	Hydrated manganous oxide formed after 27 min.
Condition of deposit	One fourth of area metallic, ¾ of area black and somewhat rough.	Initially smooth and bright and well-adhered.	Entire area smooth and silvery in color, though not mirror-like. Treed on edges.

By employing a manganese metal anode in place of a platinum anode, the formation of a precipitate in the electrolyte is greatly retarded. However, the flaking of black manganese dioxide, carbon, silicon dioxide and ferric oxide from the anode fouled the electrolyte to an appreciable extent. In order to overcome this, a diaphragm separating the electrolyte into anode and cathode chambers was employed, and it was found that the separation of the anolyte and catholyte caused a plate lighter in color and freer from inclusions of manganese dioxide than was obtained previously.

In further studies of chloride electrolytes, particularly to note the influence of the concentration of manganese in the electrolyte, tests were made over a range from about 50 grams $MnCl_2.4H_2O$ up to a concentration represented by saturation at 25° C. In these tests, current densities of both 20 and 25 amperes per square decimeter were used with soluble manganese anodes and copper cathodes. Concentrations in the vicinity of 300 grams of hydrated manganese chloride having shown especially good results, a test was made in a divided cell, using this manganese concentration along with 30 grams per liter of ammonium chloride. At a current density of 20 amperes per square decimeter, a very smooth, bright, silver-white deposit was obtained that was 0.3 millimeter thick and adhered tightly to the cathode; there was some treeing on the edges. Under the optimum conditions noted below, current efficiencies were obtained in these tests ranging from 70 to 80%.

The effect of agitating the electrolyte in cells containing diaphragms and in other cells not containing diaphragms was studied. It was found that in divided cells moderate stirring of the catholyte greatly improved the appearance of the deposit to give a silver-white smooth plate. These beneficial results increased with greater agitation up to a point at which the effect became detrimental. The effect of agitating the electrolyte is to remove the hydroxyl ions which accumulate in the neighborhood of the cathode and which presumably attack the deposited metal and form metallic hydroxides or hydrated oxides which may be occluded in the deposit. In these tests also, high current efficiencies in terms of deposited manganese were obtained, as high as 77%.

The optimum conditions of electrolysis for the $MnCl_2+NH_4Cl$ electrolyte as established by the foregoing and other tests are as follows:

Anode	Commercial (96 per cent pure) manganese.
Cathode	Carefully cleaned and buffed copper sheet.
Cell	Catholyte and anolyte separated by a porous diaphragm.
Electrolyte	Solution containing 300 to 400 g./l. $MnCl_2.4H_2O$ and 30 g./l. NH_4Cl.
Cathode current density	20 amp./dm.^{2}
Voltage	1.0 to 4.5 volts.
Stirring of catholyte	Sufficiently vigorous to insure rapid motion of the electrolyte past the surface of the cathode.
Temperature	26° C.
Anode current density	Below 40 amp./dm.^{2}

By carrying out the process under optimum conditions, metallic manganese of 100 per cent purity may be deposited from chloride electrolytes on copper cathodes as good adherent plates of smooth silver-white metal which up to at least 0.3 mm. thickness are devoid of crystals visible to the unaided eye. These plates are capable of a very high polish and have a scratch hardness of 5.5 to 6.0 on the Mohs' scale.

Although the optimum current density is about 20 amperes per square decimeter, this may be varied somewhat. On the other hand, too low current densities give basic cathode deposits without metallic luster. Too high current densities give black cathode deposits, which are characterized by a lack of adherence. For a high purity product, the current density should preferably be maintained between about 15 and 25 amperes per square decimeter.

Electrolyte temperatures below 10° C. require high voltages and give poor deposits. Temperatures above 40° C. permit the use of low voltages but give foul, poorly adherent plates. The best deposits are obtained in the neighborhood of 26° C. and the preferred range is from about 20 to 35° C.

Numerous studies have also been made using manganese sulphate electrolytes. Pure, smooth, coherent, silver-white manganese deposits, not visibly crystalline and of thickness comparable to that obtained with chloride baths, may be secured. These plates resist atmospheric oxidation and the corrosive action of laboratory fumes for several years. Cathodic efficiencies of 60–75% are normal, using an electrolyte of 100 g./l. $MnSO_4.4H_2O$ plue 75 g./l. $(NH_4)_2SO_4$ plus 60 g./l. NH_4CNS, a cathode current density of 25 amp./dm.^{2}; a pH of 4.0 to 5.5 and a bath temperature of 25° C.

In carrying out the work on manganese sulphate electrolytes, a conventional type of cell equipped with a glass stirrer was usually used. Since the soluble manganese anode had been shown by the tests in chloride electrolytes to possess numerous advantages, it was also employed in much of the work with sulphate electrolytes. Its performance was, however, not entirely satisfactory, so that among the tests in sulphate electrolytes were included, some with insoluble anodes, among these being lead, lead sulphate, manganese dioxide, platinum, carbon and graphite.

The lead, lead sulphate and platinum anodes produced basic manganese precipitates, probably due to the high oxygen over-voltage exhibited by these anode materials. The manganese dioxide anodes were found to have very high electrical re-

sistance. Commercial carbon rod material, when used as anode, disintegrated rapidly. When graphite anodes were used, conductivity was favorable and disintegration was slow. However, graphite anodes as well as other insoluble anodes are unsuited to depositing large quantities of metal without adjustment and replenishment of the electrolyte.

Again it was observed that the soluble manganese anodes went into solution faster than the current equivalent and thereby enriched the manganese content of the bath beyond the optimum concentration. Thus, while this soluble anode was highly advantageous, it was not completely satisfactory for long time continuous deposition.

We discovered, however, that highly satisfactory results could be obtained by employing both a soluble manganese anode and an insoluble anode, such as graphite, in the same bath. By regulating the amount of electric current supplied to each type of anode, we could keep the pH value of the bath substantially constant. Sufficient current was passed through the soluble manganese anode barely to maintain the manganese content of the bath. The remainder of the current was passed through the insoluble graphite anode. By varying the adjustment of these two current strengths to meet other variables, such as temperature, agitation, addition agents, etc., it was readily possible to control both the hydrogen ion concentration and the manganese content of the bath.

The figure illustrates in a diagrammatic manner the arrangement of the apparatus, when employing both an insoluble and a soluble manganese anode. A soluble manganese anode 2, an insoluble graphite anode 3 and a copper cathode 4 are immersed in a manganese sulphate electrolyte contained in a cell 5. The cell is provided with a stirrer 6. The soluble anode 2 is connected by a line 7 provided with a variable resistance 8, a line 9, a lamp bank 10 to one branch 11 of the positive electrical conductor 12. The insoluble anode 3 is similarly connected by a line 13, a variable resistance 14, line 15, lamp bank 16 to a branch line 17, which also is connected to the positive electrical conductor 12. The cathode 4 is connected to the negative electrical conductor 18. The conductors 7, 13 and 18 are provided with ammeters 19, and a volt meter 20 is arranged in the line 21, which connects the conductors 18 and 13.

In carrying out the work employing a combination of soluble and insoluble anodes, a series of electrolytes was prepared to contain from 50 to 600 g./l. of $MnSO_4.4H_2O$. For each of these electrolytes another series was prepared in which the amount of $(NH_4)_2SO_4$ present was varied from zero to 150 g./l. The manganese deposits obtained indicated that the solution containing 100 g./l. of $MnSO_4.4H_2O$ with 75 g./l. of $(NH_4)_2SO_4$ was most satisfactory. Its hydrogen ion concentration was more readily controlled than in the others; less gassing occurred at the electrodes; and treeing of the deposit was minimized. NH_4Cl was equally as effective as $(NH_4)_2SO_4$ in manganese sulphate baths in assisting maintenance of metallic manganese deposits of the desired quality.

The effect of the variation of cathode current density was next investigated. The values used ranged from 5 amp./dm.^{2} to 50 amp./dm.^{2}. Under normal conditions, a cathode current density of 25.0 amp./dm.^{2} proved the most satisfactory. Good results were obtained over the range from 20 amp./dm.^{2} to 30 amp./dm.^{2}.

A study of the effect of the temperature of the electrolyte showed that good deposits were possible between 15° to 30° C., with best plates at temperatures around 25° C. At higher temperatures deposits showed rather pronounced darkening and a tendency to become rough and to develop trees.

In general, the best results were obtained when stirring produced just enough agitation to prevent the hydrogen evolved from adhering to the cathode or from sliding up its face.

In order to allow free circulation of the electrolyte and at the same time to avoid bath pollution, diaphragms were employed to separate the anolyte and catholyte.

This deposit exhibited a silver-white, bright appearance, with extreme smoothness and no spotting. As deposition continued, treeing developed at the edge of the cathode, but the main body of the plate was very smooth and silvery-white. Cell voltages had become fairly constant at 4.2 volts. This smooth, white metal did not tarnish in air when dry and showed little tendency to react with the electrolyte after the current was interrupted.

A large number of addition agents of various types were employed with the manganese sulphate electrolyte. It was found that ammonium sulphate and ammonium thiocyanate together exerted a decidedly beneficial effect on the nature of the deposits, including a marked reduction in the tendency to treeing. Of the former, 75 grams per liter and of the latter 60 grams per liter were found to be optimum concentrations.

With an electrolyte containing 100 g./l. of $MnSO_4.4H_2O$, 75 g./l. $(NH_4)_2SO_4$ and 60 g./l. of NH_4CNS, best results were obtained at a pH range of 4.0 to 5.5, although good deposition occurred over a much wider range. Both the pH value and the metal content of the bath are readily controlled by varying the ratio of the current passing through the soluble and insoluble anodes. The ratio of current passing through the soluble manganese anode to current passing through the insoluble graphite anode was in many cases about 1 to 8, although this ratio may vary considerably, depending upon addition agents, temperature of electrolyte, composition of the electrolyte and other factors.

The optimum conditions for producing a compact, tightly adherent silver-white electro-deposited manganese from this bath were found to be as follows:

Cathode	Carefully cleaned and buffed copper sheet.
Soluble anode	Commercial (96 per cent pure) manganese rod.
Insoluble anode	Acheson graphite rod.
Electrical circuit	Suitable for independent adjustment of current through each anode.
Diaphragm	Anodes enclosed in cloth bags.
Electrolyte	100 g./l. $MnSO_4.4H_2O$ plus 75 g./l $(NH_4)_2SO_4$ plus 60 g./l. NH_4CNS.
Cathode current density	25 amp./dm.^{2}
Initial anode current density (soluble)	5 amp./dm.^{2} max. 35 amp./dm.^{2}
Initial anode current density (insoluble)	30 amp./dm.^{2}
Initial current ratio	Soluble: insoluble—1:5 to 1:8
Agitation	Sufficient to remove hydrogen from cathode surface.
pH range	4.0 to 5.5
Bath temperature	25° C.
Voltage—from soluble anode	4.5 to 8
Voltage—from insoluble anode	11 to 12

The combination of soluble and insoluble anodes may likewise be employed with other elec-

trolytes. The optimum conditions for a manganese chloride bath are as follows:

Electrolyte	A solution containing 300 to 400 g./l. $MnCl_2.4H_2O$ to 60 g./l. NH_4Cl.
Cathode	Carefully buffed and cleaned copper sheet.
Anode (insoluble)	Acheson graphite rod.
Anode (soluble)	Commercial (96% pure) Mn.
Electric circuit	Suitable for independent adjustment of current through each anode.
Cell	Anolyte and catholyte separated by cloth diaphragms.
Current density (cathodic).	20 amp./dm.^{2}
Initial anode current density (soluble).	20 to 30 amp./dm.^{2} max. 40 amp./dm.^{2}
Initial anode current density (insoluble).	15 to 25 amp./dm.^{2}
Voltages (from soluble anode).	4.5 to 5.5 volts.
Voltages (from insoluble anode).	7.5 to 12 volts.
Agitation	Sufficiently vigorous to insure rapid motion of electrolyte past cathode and anode chambers.
Temperature	26° C.
Initial ratio of current (soluble: insoluble).	1:2.

With these optimum conditions and the combination of soluble and insoluble anode current efficiencies as high as those obtained with the soluble anode alone, can be secured, namely 60 to 80%.

The use of a diaphragm, although preferred, may be dispensed with in some cases, if provision is made for removing the sediment which may accumulate.

Although the preferred cathode metal is copper, manganese can be plated on metals of widely divergent nature, such, for example, as tin, cadmium, nickel, platinum, iron, zinc, aluminum and lead.

Electrodeposits of manganese described in the prior art have been mentioned as being readily oxidizable. In our studies of electrolytes and methods for depositing manganese metal, we have confirmed these reports and noted that the electrodeposits frequently will acquire dark oxide surfaces in considerably less than one minute after removal from the electrolyte. In contrast with these, deposits of manganese produced in accordance with our method are not readily oxidized. In fact, they are distinctly corrosion resistant and have maintained a good appearance in the atmosphere and also in the atmosphere of a chemical laboratory for five years or more. The degree of corrosion resistance is not equal to that of chromium or of steels rich in chromium or chromium and nickel but more nearly approaches that of copper alloys, such as Monel metal, and is definitely greater than that of iron or, in some cases, of copper. We believe that this desirable degree of corrosion resistance is due to the very high purity and compactness and possibly other properties of our electrodeposit as previously described.

A thorough investigation has been made of the effect of variation of anode current densities. It has been established that optimum conditions can be maintained over anode current density zones pertinent to each electrolyte under the conditions selected. Specific examples under optimum conditions are as cited above.

Although the optimum pH value of the solutions will vary according to the type of manganese salt employed, the type of addition agents if they are used and upon other factors, we have found that the pH value should in all cases be between about 3 and 7.3.

The invention is not limited to supplying all of the manganese from the soluble anode or from the electrolyte as originally made up. Manganese salts may be added to the bath from time to time to assist in maintaining the desired concentration of manganese.

It is understood that the invention is not limited to the preferred embodiment or manner of practicing the invention, but that it may be otherwise embodied or practiced within the scope of the following claims.

We claim:

1. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing manganese sulphate, said solution also containing an ammonium salt of the group consisting of ammonium sulphate and ammonium chloride, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of the solution between about 4.0 and 5.5.

2. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing manganese sulphate and an ammonium salt, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of the solution between about 4.0 and 5.5.

3. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing manganese sulphate, an ammonium salt of the group consisting of ammonium sulphate and ammonium chloride, the solution also containing ammonium thiocyanate, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of the solution between about 4.0 and 5.5.

4. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing per liter about:

	Grams
$MnSO_4.4H_2O$	100
$(NH_4)_2SO_4$	75
NH_4CNS	60

said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of the solution between about 4.0 and 5.5.

5. The process of producing manganese, which comprises employing a soluble manganese anode and electro-depositing manganese from an aqueous solution containing manganese sulphate, said solution also containing an ammonium salt, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of the solution between about 4.0 and 5.5.

6. The process of producing manganese, which comprises employing a soluble manganese anode and an insoluble anode and electro-depositing manganese from an aqueous solution containing manganese sulphate, said solution also containing an ammonium salt, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of

the solution between about 4.0 and 5.5 by controlling the proportion of the total current which is supplied to each type anode.

7. The process of producing manganese, which comprises employing a soluble manganese anode and an insoluble anode and electrodepositing manganese from an aqueous solution containing manganese sulphate, an ammonium salt of the group consisting of ammonium sulphate and ammonium chloride, the solution also containing ammonium thiocyanate, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and a temperature of about 15–30° C., and regulating the pH value of the solution between about 4.0 and 5.5 by controlling the proportion of the total current which is supplied to each type anode.

8. As an article of manufacture, a plate of electrodeposited manganese of approximately 100% purity, which in thick deposits over 0.1 mm. in thickness and up to at least 0.3 mm. in thickness is smooth, adherent, silver-white and devoid of crystals visible to the unaided eye.

9. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing manganese salt of the group consisting of manganese sulphate and manganese chloride, said solution also containing an ammonium salt of the group consisting of ammonium sulphate and ammonium chloride, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–25 amperes per square decimeter and at a temperature of about 25° C., and regulating the pH value of the solution between about 3.0 and 7.3.

10. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing manganese chloride and ammonium chloride, said solution being substantially free from other depositable metal salts, at a cathode current density of about 15–25 amperes per square decimeter and at a temperature of about 10 to 40° C., and regulating the pH value of the solution between about 3.0 and 7.3.

11. The process of producing manganese, which comprises electrodepositing manganese from an aqueous solution containing manganese sulphate and an ammonium salt of the group consisting of ammonium sulphate and ammonium chloride, said solution being substantially free from other depositable metal salts, at a cathode current density of about 20–30 amperes per square decimeter and at a temperature of about 15–30° C., and regulating the pH value of the solution between about 3.0 and 7.3.

WILBER E. BRADT.
HAROLD H. OAKS.