

Early Development of Water Reducers in the US

An Example of Innovation, Competition and Cooperation

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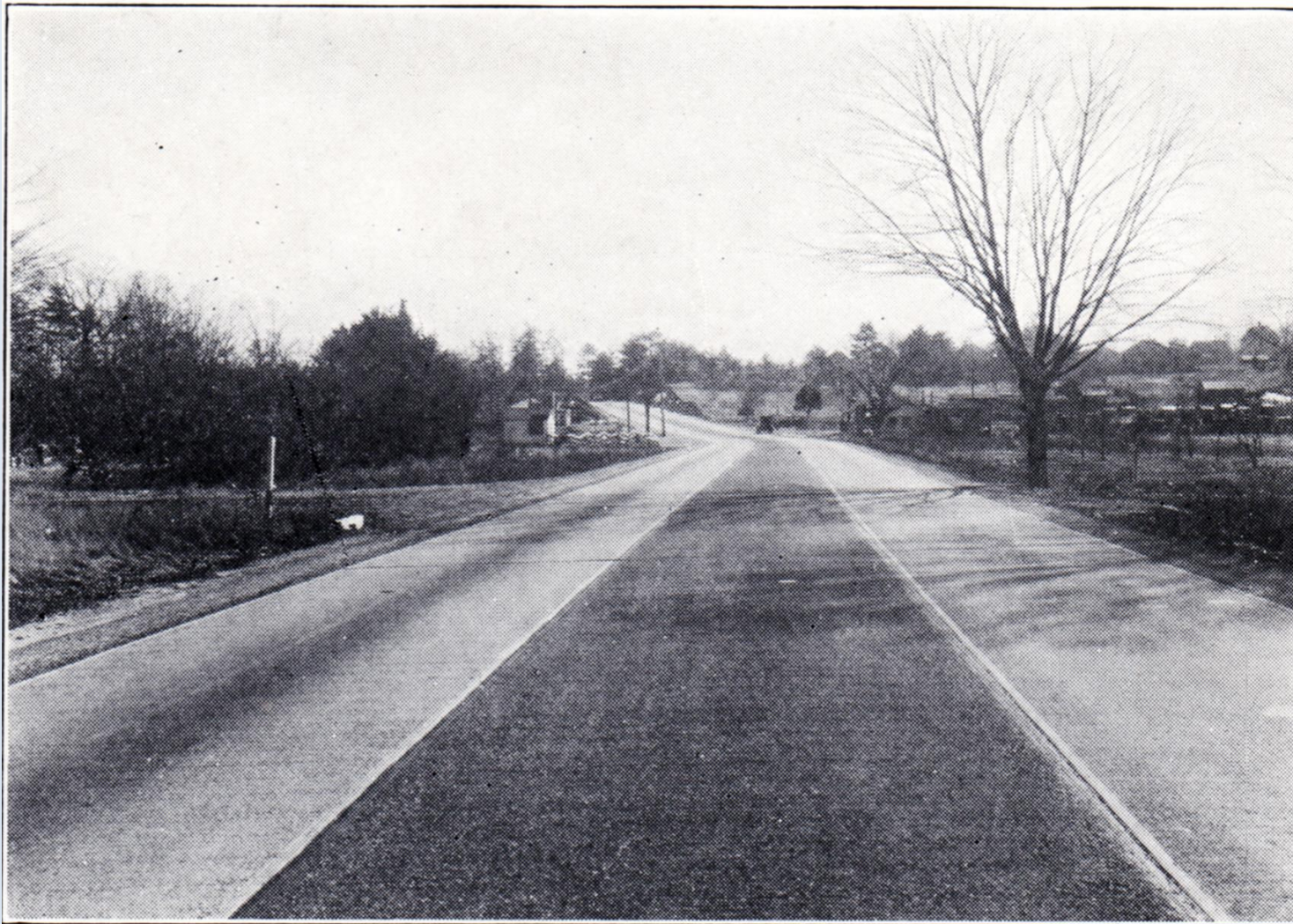
The author and Maynard S. Renner in 1985

“Let me tell you a story, Sonny.....”

“Let me tell you a story Sonny...”

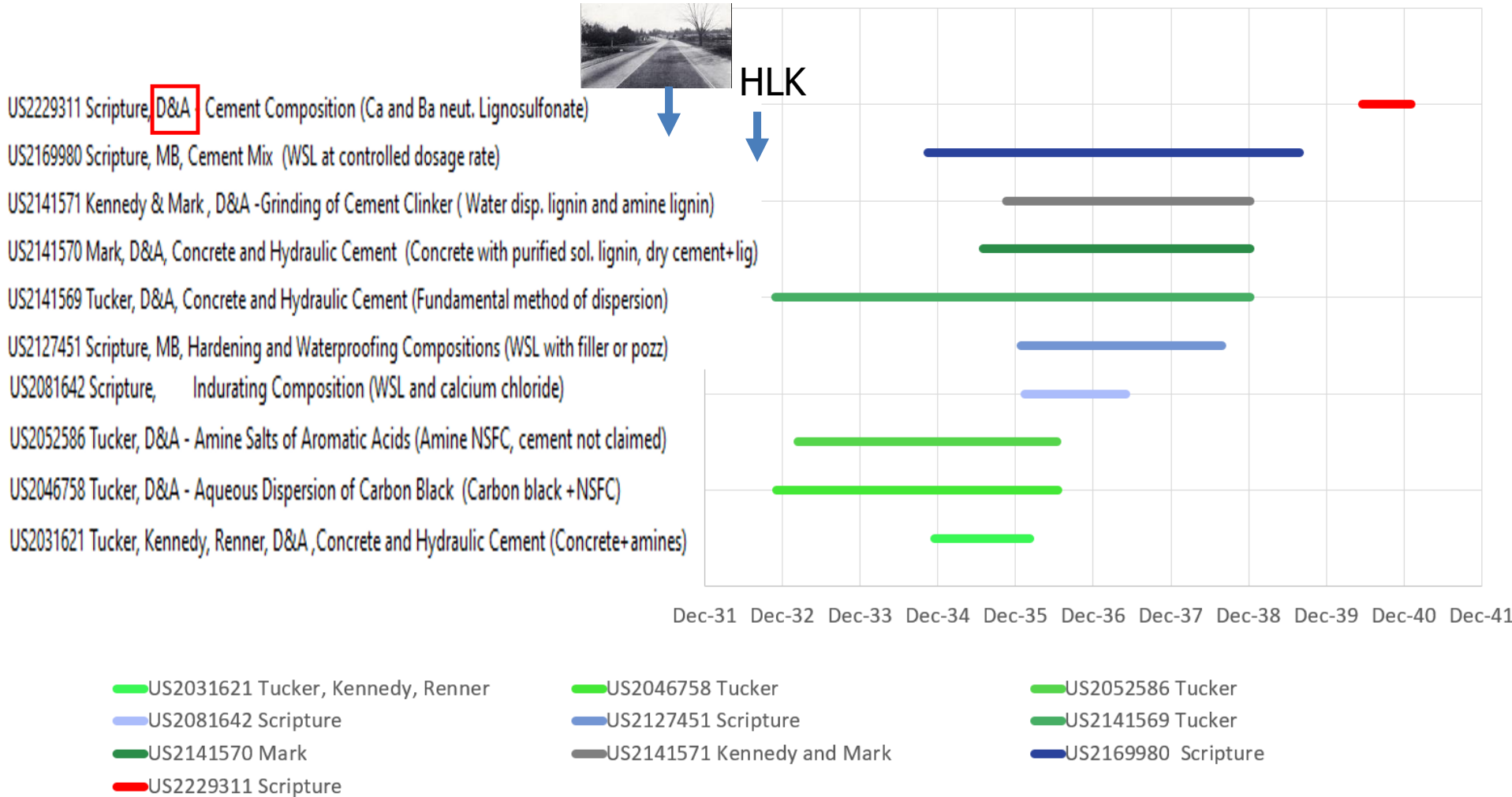
- Maynard Renner called in to meeting at Dewey & Almy in ~1930
- Cabot Corporation needed help making concrete solid black
- Maynard asked to make up solution carbon black in NSFC
- It worked
- Rest is the history we will discuss

Route 1, Avon Massachusetts, 1931



The center strip contains TDA and was laid in 1931.

Key Early D&A and MB Admixture/Additive Patents



1932 - US 2,141,569 Tucker, assigned to D&A

I claim:

1. The method of increasing the plasticity of a cement concrete mix which consists in increasing the number of discrete particles available for hydration by dispersing the individual cement particles throughout the aqueous mass by the addition of a cement dispersing agent.

2. The method of increasing the plasticity of a cement concrete mix which consists in increasing the number of discrete particles available for hydration by dispersing the individual cement particles throughout the aqueous medium by the addition of a water soluble cement dispersing agent.

3. The method of increasing the plasticity of a cement concrete mix which consists in increasing the number of discrete particles available for hydration by dispersing the individual cement particles throughout the aqueous medium by the addition of a heat-resistant cement-dispersing agent.

6. The combination of hydraulic cement and a water soluble cement dispersing agent capable of preventing the formation of agglomerations of cement particles in the aqueous medium of a suitable cement concrete mix or of breaking up any such agglomerations which may have already been formed and thereby of increasing the number of discrete particles available for hydration.

7. The combination of dry hydraulic cement and intimately admixed therewith a water soluble dispersing agent which is substantially non-foaming and is capable of preventing the formation of agglomerations of cement particles in an aqueous medium and of dispersing any which may have been already formed and thereby of increasing the number of discrete particles available for hydration.

14. The process of preparing concrete which comprises mixing cement, aggregates, and water in the presence of a soluble compound obtained by condensing formaldehyde with an aromatic sulfonic acid.

- Dispersion

1934 - US 2,031,621 Tucker, Kennedy, Renner – D&A

What is claimed is:

1. That process for the preparation of concrete which includes mixing hydraulic cement, aggregates, and water in the presence of triethanol amine.

2. That process for the preparation of concrete which includes mixing hydraulic cement, aggregates, and water in the presence of diethanol amine.

3. That process for the preparation of concrete which includes mixing hydraulic cement, aggregates, and water in the presence of triisopropanol amine.

4. As a new composition of matter dry hydraulic cement and a salt of a hydroxy-alkyl amine in intimate admixture therewith.

12. As a new composition of matter, hydraulic cement concrete containing an ethanol amine and strengthened thereby.

13. As a new composition of matter, hydraulic cement concrete containing triethanol amine and strengthened thereby.

15. As a new composition of matter, concrete which contains a salt of a hydroxy-alkyl amine.

16. That process for the preparation of concrete which comprises mixing hydraulic cement, aggregates and water in the presence of a hydroxy-alkyl amine.

17. That process for the preparation of concrete which comprises mixing hydraulic cement, aggregates, and water in the presence of a salt of an ethanol amine.

- Ethanolamines

1935 - US 2,141,570 Mark, assigned to D&A

I have discovered that certain agents not mentioned by Dr. Tucker possess to an even more marked degree the property of dispersing cement particles and of producing high slump in concrete mixtures. In contradistinction to the agents mentioned by Dr. Tucker, which are comparatively costly, the substances which I may use are found in obnoxious wastes from paper mills and may be obtained very cheaply. These are the commercially pure, water-soluble derivatives of lignin.

- Purified lignin

What I claim is:

1. Structural concrete of commercially acceptable compressive strength containing hydraulic cement and a water soluble derivative of lignin which has been separated by chemical treatment from other constituents present in the wastes of pulp recovery processes.
2. A dry cement having materially increased workability in the wet state and producing structural concretes of normal compressive strengths comprising hydraulic cement and a salt of lignin sulphonic acid separated by chemical treatment
8. As an intermediate product, plastic cement concrete containing hydraulic cement and possessing high workability and producing structural concretes of commercially acceptable compressive strengths by virtue of the presence therein of a water-soluble derivative of lignin which has been separated by chemical treatment from other constituents present in the wastes of pulp recovery processes.

1940 - US 2,229,311 Scripture assigned to D&A

I claim:

1. A cement composition comprising a mixture of cement and cellulose waste liquor modified by precipitation of sulphate ions therefrom through addition of a soluble alkaline earth compound in such amount that substantially no alkaline earth compound capable of accelerating the set of concrete remains after reaction.

2. A plasticizing and indurating composition for use in the making of concrete comprising cellulose waste liquor modified by the addition of such an amount of a soluble alkaline earth compound as to remove sulphate ions therefrom by precipitation of alkaline earth sulphates without leaving any substantial excess of alkaline earth compound capable of accelerating the set of concrete.

- Lignin plus NON-ACCELERATING level of alkaline earth salts

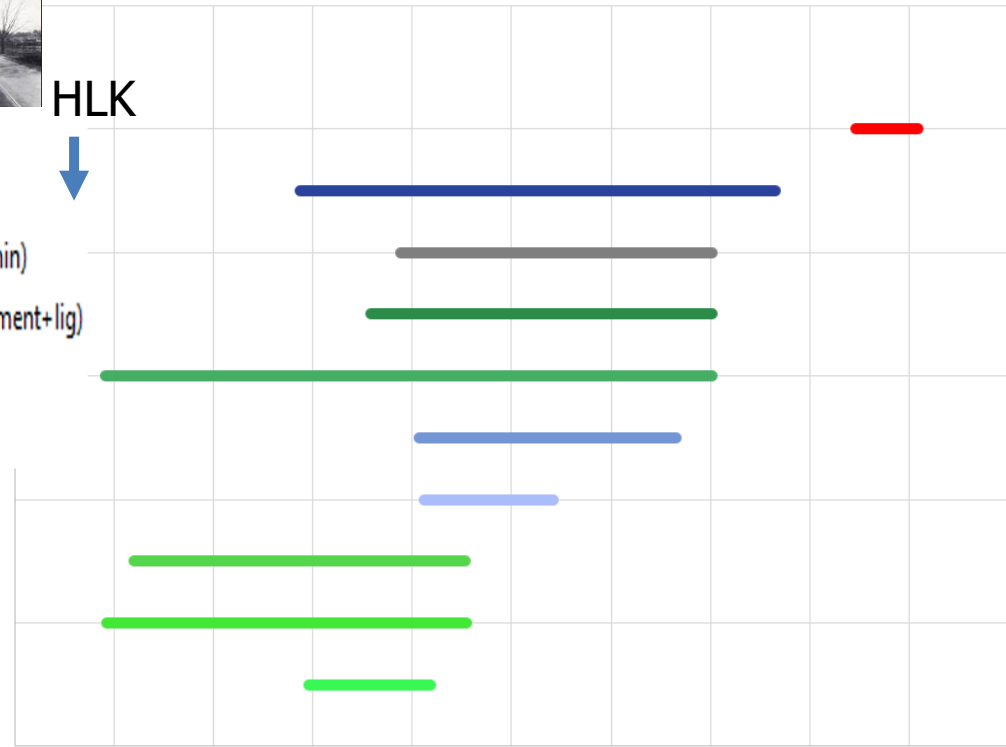
Now let's look at the Master Builders Patent timeline

Key Early D&A and MB Admixture/Additive Patents



HLK

- US2229311 Scripture, D&A Cement Composition (Ca and Ba neut. Lignosulfonate)
- US2169980 Scripture, MB, Cement Mix (WSL at controlled dosage rate)
- US2141571 Kennedy & Mark, D&A -Grinding of Cement Clinker (Water disp. lignin and amine lignin)
- US2141570 Mark, D&A, Concrete and Hydraulic Cement (Concrete with purified sol. lignin, dry cement+lig)
- US2141569 Tucker, D&A, Concrete and Hydraulic Cement (Fundamental method of dispersion)
- US2127451 Scripture, MB, Hardening and Waterproofing Compositions (WSL with filler or pozz)
- US2081642 Scripture, Indurating Composition (WSL and calcium chloride)
- US2052586 Tucker, D&A - Amine Salts of Aromatic Acids (Amine NSFC, cement not claimed)
- US2046758 Tucker, D&A - Aqueous Dispersion of Carbon Black (Carbon black +NSFC)
- US2031621 Tucker, Kennedy, Renner, D&A ,Concrete and Hydraulic Cement (Concrete+amines)



Dec-31 Dec-32 Dec-33 Dec-34 Dec-35 Dec-36 Dec-37 Dec-38 Dec-39 Dec-40 Dec-41

- █ US2031621 Tucker, Kennedy, Renner
- █ US2046758 Tucker
- █ US2052586 Tucker
- █ US2081642 Scripture
- █ US2127451 Scripture
- █ US2141569 Tucker
- █ US2141571 Kennedy and Mark
- █ US2169980 Scripture
- █ US2141570 Mark
- █ US2229311 Scripture

1934 – US 2,169,980 Scripture, assigned to MB

What I claim is:

1. A mortar or cement mix containing the ingredients of waste sulphite liquor in substantially the proportion provided by the addition to the mix of from one-half pint to one and one-half pints of waste sulphite liquor per sack of cement.

2. A concrete comprising a mixture of hydraulic cement and aggregate, and containing the ingredients of waste sulphite liquor in substantially the proportion provided by the addition to the mix of from one-half pint to one and one-half pints of waste sulphite liquor per sack of cement.

4. As an intermediate product, plastic cement concrete containing hydraulic cement and the water soluble constituents of waste sulphite liquor, which render the cement particles mutually repellant in the aqueous medium of a suitable concrete mix, thereby increasing the number of discrete particles therein for hydration, said plastic concrete possessing high workability and producing structural concretes of commercially acceptable compressive strengths by virtue of the presence therein of the constituents of waste sulphite liquor.

6. As an intermediate product, a plastic cement mix comprising hydraulic cement having mixed therewith the water soluble constituents of waste sulphite liquor, and having the physical characteristics that when in an aqueous medium the particles disperse substantially completely, producing high workability, and, upon hydration, produce commercially acceptable compressive strengths.

7. A dry cement having materially increased workability in the wet state and producing structural concretes of normal compressive strengths comprising hydraulic cement and the water soluble constituents of waste sulphite liquor, which increase the number of discrete particles available for hydration by dispersing the individual cement particles throughout the aqueous mass.

- Waste sulfite liquor = non-purified lignin
- Mentions dispersion but does not claim it per se

1936 – US 2,127,451 Scripture, assigned to MB

1. A mortar or concrete mix comprising hydraulic cement, aggregate, a finely divided non-hydraulic filling material, and finely divided waste sulphite liquor residue in such proportions that the waste sulphite liquor residue shall be present in the mix in the proportion of .05% to .3% by weight of the cement.

2. A mortar or concrete mix comprising hydraulic cement, aggregate, a finely divided non-hydraulic pozzuolanic material, and finely divided waste sulphite liquor residue in such proportions that the waste sulphite liquor residue shall be present in the mix in the proportion of .05% to .3% by weight of the cement.

- Waste sulfite liquor = non-purified lignin
- Adds in pozzolan in claims – mentioned but not claimed in US 2,169,980

1936 – US 2,081,642 Scripture , but NOT assigned to MB?

A considerable number of chemical substances have been found effective for dispersing various finely divided solid materials in water. However, a dispersing agent effective for dispersing materials in one mixture may be relatively ineffective in another mixture. In the case of concrete mixes, a considerable number of substances which have been identified as dispersing agents for cer-

What I claim is:

1. An indurating composition for concrete or mortar, comprising waste sulphite liquor and calcium chloride.

2. An indurating composition for concrete or mortar, comprising a mixture of dried waste sulphite liquor residue and calcium chloride.

3. An indurating composition for concrete or mortar, comprising waste sulphite liquor, in an amount equivalent to .15% to .5% of dry waste sulphite liquor residue by weight of the cement, calcium chloride in an amount of .5% to 2.5% by weight of the cement, and a finely divided non-hydraulic filling material.

8. An indurating composition for concrete or mortar, comprising a mixture of dried waste sulphite liquor residue, calcium chloride, and finely divided pozzuolanic material.

9. The hereindescribed method of increasing the workability of a concrete mix containing water in a given ratio, which comprises incorporating in the mix the solids in waste sulphite liquor equivalent to .15% to .5% of dry waste sulphite liquor residue by weight of the cement and .5% to 2.5% of calcium chloride by weight of the cement.

10. A concrete mix containing waste sulphite liquor in a proportion which greatly increases the workability of the mix with a given amount of water, but which would normally decrease the strength of the concrete, together with an electrolyte which accelerates the setting of the cement and which, in the presence of waste sulphite liquor, increases the strength of the concrete without decreasing the workability of the mix, said electrolyte being one of a group of accelerating agents which includes water soluble metal chlorides.

- Clear discussion dispersion
- Waste sulfite liquor + calcium chloride

1951 - US 2,690,975 Scripture, assigned to MB

What are believed to be the first cement dispersing agents known to the art were disclosed in U. S. Patent No. 2,141,569, granted to George R. Tucker, December 27, 1938. These compositions are organic compounds of the type resulting from the condensation of aromatic sulphonic acids with formaldehyde or higher alkyl aldehydes, and optionally neutralizing the reaction product with an alkali or alkaline earth hydroxide to produce a soluble salt form of the condensation product. The most conveniently produced com-

Another class of cement dispersing agents consists of various waste sulfite liquor derivatives in which the active ingredient is a soluble salt of lignosulphonic acid. My U. S. Patent No. 2,169,980, granted August 15, 1939, discloses

Having described my invention, I claim:

1. A cement composition comprising an hydraulic cement, from about 0.05% to 0.25% by weight of the cement of desugarized waste sulfite liquor solids, and from about 0.05% to 0.20% by weight of the cement of a member of the class consisting of the water-soluble products of condensation of sulfonated aromatic hydrocarbons with aliphatic aldehydes and the water-soluble salts of said products.

- Acknowledges Tucker: “What is believed to be the first cement dispersing agents known to the art were disclosed in U.S. Patent No. 2,141,569, granted to George R. Tucker.”
- Claims Purified lignin + NSFC

Timeline of patent filings

- 1932 – D&A - concept of dispersion to reduce water, improve strength
- 1934 – MB - use of waste sulfite liquor lignin to disperse cement
- 1934 – D&A - ethanolamines as strength improvers
- 1935 – D&A - lignin treated (purified) by any chemical process
- 1936 – MB - dispersion to enable non hydraulic fillers and pozzolans
- 1936 – Scripture - waste sulfite liquor and Calcium Chloride
- 1940 – D&A (Scripture) - lignin with dose of CaCl_2 too low to accelerate
- 1951 – MB - Attributes first use of dispersing agent to Tucker of D&A

What appears to have happened

- D&A filed on the idea of water reduction through dispersion
- MB filed on waste sulfite liquor, but needed access to dispersion idea
- D&A filed on purified lignin
- MB needed access to purified lignin
- MB did not want to give access to combinations with calcium accelerators
- D&A happy to live with ethanolamines instead of calcium chloride
- But D&A needed calcium lignin, so Scripture assigned combinations where CaCl_2 concentration is too low to accelerate to D&A
- Critical patents were cross-licensed (??)
- And the industry has profited by improved concrete ever since

Learnings

- Coincidence of a family relationship brought the question of how to disperse carbon black in concrete to just the right people
- The work was quickly done yielding the desired result, but the critical element was recognizing the other benefits
- Opportunity was realized and quickly and significantly invested in
- Patents were correctly written, interferences understood, and resolution decided based on opportunity, not ego
- Competition, and then the cooperative resolution of that competition, rapidly advanced concrete technology

In Conclusion

One other interesting aside. This technology came from a company formed by two men dedicated to supporting the US Army, which was helping France and Britain in World War I. This business section of that company is now part of Saint-Gobain, a 350+ year old French company. Coincidence??

(By the way if anybody from Master Builders has any details of that early 1930s interaction, let's get together at the next ACI meeting. I'll buy.)