

History of Paint Science and Technology

This is a summarised history of the paint industry since 1920, approximately, and sometimes before. It includes some of the important dates for the development of crucial scientific understanding as well for more general elements of polymer science. It has been arbitrarily assembled through the limited reading and incomplete understanding of the author, who tries to improve and extend this as more time and information becomes available. There are dates earlier than 1930; these have been inserted due to their significance in establishing either the science or technology for what came later. The amount of information is less for dates after ~1980 since it seems to me that this is the “modern era” of paint technology that is still reasonably current and I have yet to decide about what has been really significant – suggestions are welcome.

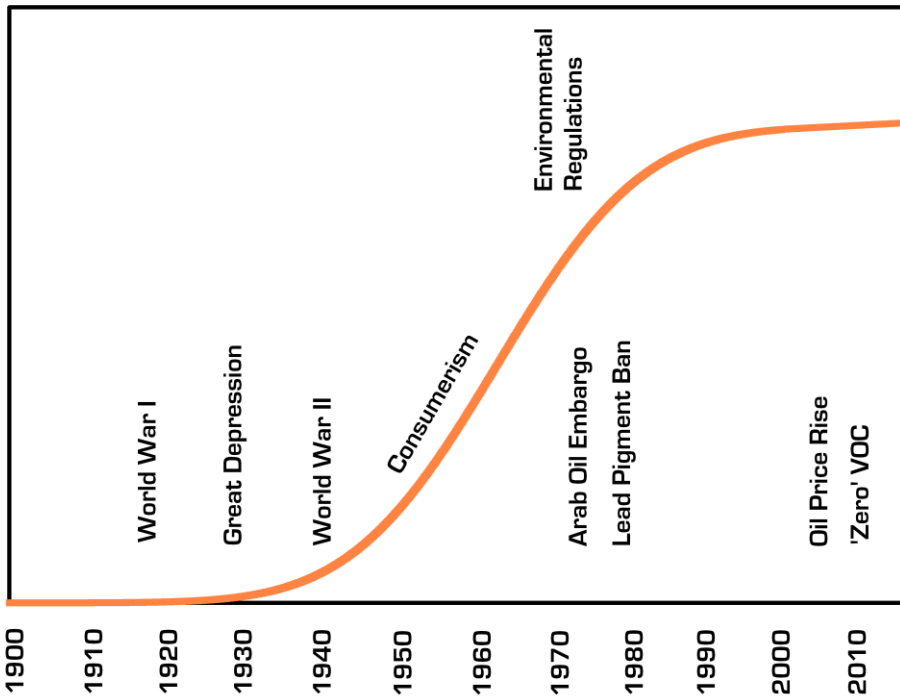
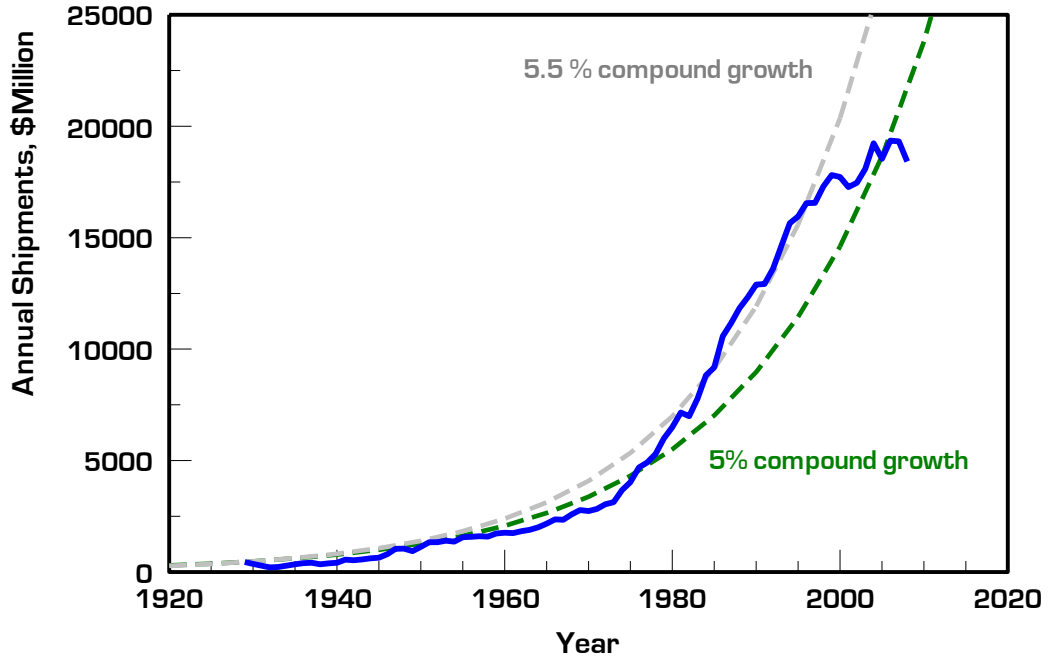
The sources for the entries are in the bibliography if they are general in nature. Sometimes more than one source was used for an entry and sometimes there was some disagreement in fact or timing that I have attempted to rationalise.

This history is in three sections at present. The first deals with polymers, polymer science and their impact on coatings technology, since that is where most of the focus resides. The current emphasis here is on water-borne latex paint systems. There is a very limited section on the development of analytical characterization techniques, followed by a section that gives a timeline for the development of pigments.

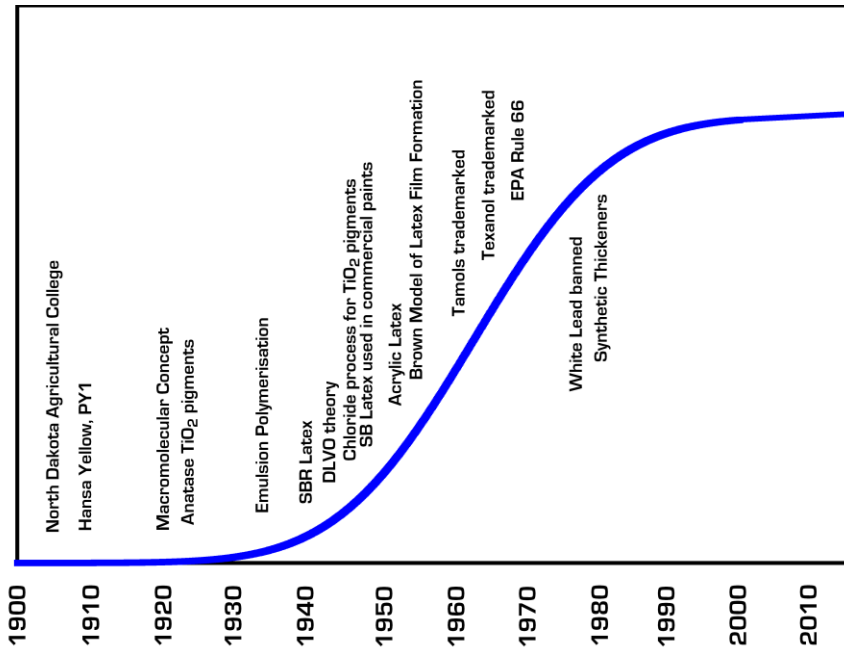
Three graphs here track the rise of paint technology overall according to my impressions. I have used a basically sigmoidal shape, in common with other presentations of technology maturation [P. A. Roussel, *Research Management*, 27(1), 29 (1984)]. The rise of paint technology is the same in each graph, but in one I have entered some of the major, external, historical factors, and in the other I have included some of the major technology developments for acrylic latex paint and alkyd paint (although the curve is my visualization of the whole of paint technology).

In simple commercial context, the first graph below shows how, in the US at least (from Census Bureau data), the paint industry continues to be important and grows with the economy and suffers with the economy. In fact, as long as one needs to control the appearance of useful or amusing things, or they need protection, we will always need paint. Even modern nano- or bio-materials are more often employed as coatings than any thing else, so I cannot see the market for paints or other coatings diminishing.

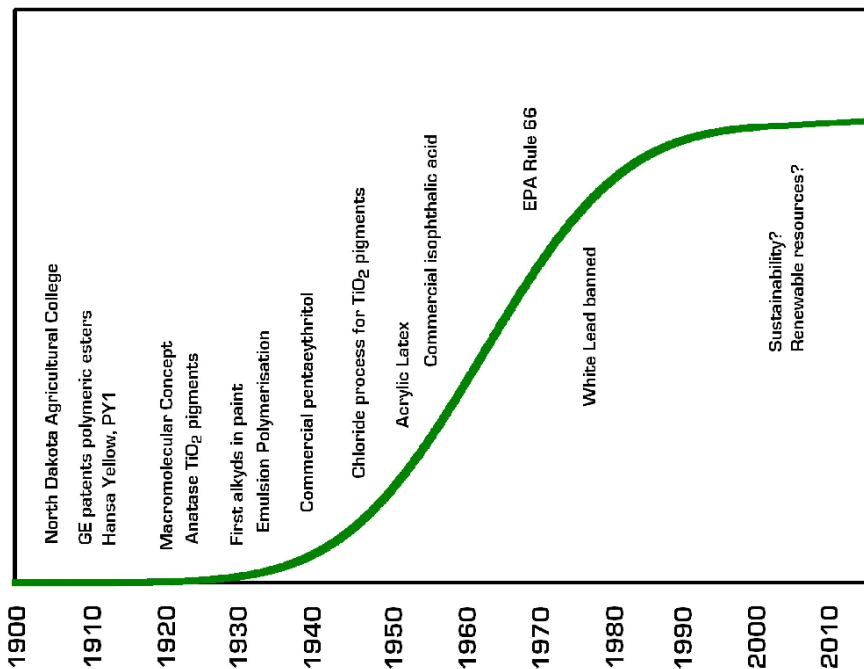
U S Annual Shipments of Paints, Varnishes and Lacquers, \$Millions
 Updated July 2009.



In contrast with the sales figures before, the above graph places the rise of paint technology in the context of some of the external influences.



This graph above traces the rise of latex (emulsion) paint technology in terms of what I believe are some of the principal technical, scientific events. Only the colour of the curve changed from the previous graph.



The last graph labels the rise in paint technology with events that were important from the point of view of alkyd paint. I chose green for the curve because oil and alkyd paints use some renewable resources as feedstock.

In the US, the existence over the years of many hundreds (actually > 1000) small companies that made paint was the costs and difficulties of shipping the finished paint far afield so companies tended to be very regional in outlook. This has changed in the modern era now that suppliers' and manufacturers' distribution infrastructure has improved.

The author apologises for the inconsistent style, but hopes that it will improve as additional data arrives that forces him to rewrite the content.

Stuart Croll, December, 2009.

Historical Dates

1844

Charles Goodyear discovers that heating sulphur containing natural rubber produces a very elastic solid. This is “vulcanization” and the first crosslinked polymer.

1846

‘Gun cotton’ (cellulose trinitrate) was patented by Schönbein, although one can probably trace nitrated cellulose back to Henri Braconnot (France) in 1832.

1865

Alexander Parks (England) treats cellulose nitrate with other materials (that we now know were plasticizers) to make (and patent) ‘Parkesine’, with which he could make some simple articles for display for the Royal Society of Arts. Later (1869) patented by J. W. and H. Hyatt in USA (the bounders!) when they improved Parkesine as Celluloid, being the first commercial plastic that modern users would recognize.

1905

Paint and coatings research starts at North Dakota Agricultural College, now North Dakota State University.

Phenol-formaldehyde resins (‘Novolac’ resin) made by Leo Hendrik Baekeland, patented in 1907: “Method of Making Insoluble Products of Phenol and Formaldehyde”. These are better known as Bakelite.

A. H. Munsell, a painter and art teacher, publishes his color notation system; the first useful description of a colour space.

1912

Dispersion polymerization of isoprene patented in Germany by Kurt Gottlob (German patents 254 & 255). Used egg albumin or starch as emulsifier.
Acrylic resins patented.

1913

Rosin-modified phenolic resins

1914

Polyvinyl acetate patented by Klatte and Rollet.

1914-18

First synthetic detergents developed in Germany during World War I. They were short-chain alkyl naphthalene sulphonates. Similar materials are still used.

1916

Joel H. Hildebrand makes strides in solubility theory for non-electrolytes.

1917

Staudinger presents the macromolecular concept at a meeting of the Swiss Chemical Society. He received the Nobel prize for this discovery in 1953.

1920

Staudinger publishes macromolecular concept: Staudinger, H. *Ber. Deut. Chem. Ges.* **1920**, 53, 1073

DuPont scientists make a fast-drying lacquer from nitrocellulose. Dupont had a background with nitrocellulose since it had been making it for explosives since the 1890s. Patent applied for use of Aluminium and Zinc Stearates as pigment stabilizers in oil paints (US 1,421,625 in 1922). Metal soaps had been known to help stabilize pigments for some time before this.

1922

DuPont patents nitrocellulose lacquers.

1923

Cellulose nitrate lacquers first used on cars (“Duco” from DuPont). The use came because a low viscosity resin (sprayable at useful solids) was discovered by DuPont in 1920 (see above), as opposed to the very high molecular weight resins that been investigated prior to that. This was taken up by many of the companies that later became General Motors, Chrysler and Ford. Ford most famously used it as one of the enablers for assembly line production. Previously, the oil paints had needed 3 – 6- weeks to cure and be dry to the touch on the vehicle.

1925

BASF (Glasurit-Werke) introduce nitrocellulose car paints in Europe. “Tamol” name first used for compounds in dyeing, tanning and textile industries (see 1968).

1921 – 1925

Alkyd resins introduced but they were slow drying, even when baked. Note: one can trace polyesters back to Berzelius who condensed glycerol tartrate in 1847. Maleated rosin varnish gums introduced.

1920s

Spray guns developed.
R. H. Kienle of GE develops unsaturated alkyds.

1926

Paint Research Station founded in UK.
GE introduce Glyptal® resins (glycerol phthalate)
DuPont introduce alkyd resin (glycerol/phthalic anhydride/linseed oil). Alkyd modified oil paints and then alkyd paints were eventually used on cars and household appliances.

1927

R. Kienle et al. of G.E. patents alkyds, but the patent is ruled invalid in 1935 due to prior art, which enables other companies to make and sell alkyds (after 1935). Kienle was

probably responsible for the combination of the word alkyd – from the condensation of alcohols and acids.

1928

R. H. Kienle and C. S. Ferguson present a paper at an ACS meeting in September, entitled “Alkyd Resins as Film-Forming Materials. This was published in 1929 in *Ind. Eng. Chem.*

1929

W. H. Carothers (DuPont) publishes on linear polyesters, *J. Am Chem Soc.*, 51, 2560 (1929). He is generally credited with formalizing the concept of functionality, although Kienle had almost certainly been thinking along the same lines.

1930

Paul Flory starts work on molecular weight distributions (experimentally and theoretically) and shows that step-growth polymerizations follow the Gaussian distribution for molecular weight.

Rehbinder, Lagutkina, Wenstrom, gain first insights into steric stabilization of colloidal particles, *Z. Physik. Chem.* (1930).

1931

Commission Internationale de l'Éclairage, CIE, meets in Cambridge and defines the primary stimuli for colour vision to be red (700 nm), green (546.1 nm) and blue (435.8 nm). The meeting also defines several illumination standard spectra and the first standard observer.

DuPont makes TiO₂ pigment by sulphate process, having purchased the Commercial Pigments Corporation that held the patents. These pigments were sold by the Krebs Pigment and Color Corporation (a DuPont subsidiary) as TiPure® but it continued to make a TiO₂ enhanced lithopone as Duolith®.

1931-32

DuPont introduce “Dulux” as a brand name for alkyd paint. However, DuPont and Nobel collaborated in the early 1920s on explosives, as much as anything else, and Nobel used the name in Europe. DuPont and ICI (UK) started a technical collaboration in October 1929 but dissolved the association in 1952. Clearly, the name “Dulux” stayed with ICI thereafter.

Luther and Hück patent a method for making a SBR latex material (working for I. G. Farbenindustrie in Germany), US patent 1,864,078 (June 21, 1932)

1930s

Wallace Carothers at DuPont synthesizes aliphatic polyesters, polychloroprene and polyamide 6,6 (Nylon, patented 1937). Work supported the macromolecular concept and his definition of a polymer is one that fits modern usage better than Staudinger's. Herman Mark, Werner Kuhn, Eugene Guth find that polymers in solution are flexible and that viscosity is related to molecular weight of the polymer. P. Castan (Switzerland) and S. Greenlee (USA) patent epoxy resins. Triton surfactants invented by Herman Bruson (for Rohm and Haas?).

1933

National Grid for supplying electricity was established in the United Kingdom by interconnecting regional grids and was more fully integrated in 1938. Electrical power was becoming much more available during the 30s'. Plenty of coal was available in the UK and elsewhere for fuel.

1934

Mark, Kuhn and Guth generate first statistical mechanical theory for rubber elasticity.

1930 – 1935

Urea formaldehyde resins combined with alkyd resins; vinyl chloride was made useful for coatings (soluble) by copolymerizing with vinyl acetate. Ford and Chrysler use alkyd enamel topcoats.

1933

Schlack patents the first epoxy resins: diglycidyl ethers made from epichlorhydrin and bisphenol A: German Patent 676,117. Styrene-Butadiene rubber made in Germany

1935

Polyvinyl butyral made for use in wash primers.

1936

Joel H. Hildebrand identifies the square root of the cohesive energy density as a quantification of solvency.

1937

Urethane resins produced by Bayer for elastomers and foams (urea reaction produces CO₂ naturally). First commercial production of pentaerythritol – important for alkyd chemistry.

1937

Patent 2,071,250 (filed in 1931) Linear Condensation Polymers granted for the work that leads to Nylon W. H. Carothers (DuPont)

1939

Thermosetting acrylics developed by D. E. Strain (U.S. Patent 2173005 to DuPont, 1939).

1940

Melamine formaldehyde resins.

The paint roller was invented by Norman Breakey of Toronto.

1940s

Styrene-Butadiene synthetic rubber latex developed as the “Mutual Recipe” in the USA (75% butadiene, 25% styrene with a rosin soap and a little mercaptan) since isoprene did not give a useful material. Production started in 1943. This project involved a number of universities and large chemical companies in the US at the time and it is claimed that the project rivaled the Manhattan Project in size and importance

(<http://acswebcontent.acs.org/landmarks/about2.html>).

Flory develops his version of rubber elasticity theory to model the properties of crosslinked polymers (with Rehner for solvent swelling).

For some historians the “2nd Chemical Revolution” starts in this period (1st chemical revolution took place with the work of Lavoisier and Berzelius, 1780 etc)

1941 – 1945

German warplanes use urethane paints (and baffle Allies initially).

1941

Derjaguin and L. Landau, publish their version of the DLVO theory [*Acta Physicochim. (URSS)* **14** (1941) 633–662.].

First widely sold commercial water based paint: Sherwin-Williams sell ‘Kemtone®.’

The binder used casein, corn protein, rosin and a small amount of linseed oil in an emulsion with TiO₂, chalk, clay and mica.

1942

Flory and Huggins in 1942 independently [P. J. Flory, *J. Chem. Phys.*, Vol. 10, 51 (1942); M. L. Huggins, *J. Am. Chem. Soc.*, 64, 1712 (1942)] developed a theory of solubility and interactions to improve regular solution theory to include better the connected nature of polymer molecules. Originated “theta” solvent concept.

1944

Germans use waterborne paint similar to PVA, for Tiger tanks. Linseed oil was in very short supply in Germany and it was known their railway rolling-stock was also being painted with a waterborne finish. [Keith Hammond series in *PPCJ, Polymers Paint Colour Journal* Feb-July 2003]

1945

GE and Dow Corning announce silicone rubbers for gaskets etc. Silicone polymers are used in high temperature and weather resistant applications since the silicon is fully oxidized and cannot oxidize more. They have been used in a wide variety of chemical resistant applications, coil coatings etc.

UV curing patent to DuPont US patent 2367670, R. E. Christ

Pentarythritol used in alkyds instead of glycerol.

Styrenated alkyds appear.

1946

Ciba commercialises an epoxy resin.
Styrene-butadiene latex commercialized for paper coatings
UV curing ink, Inmont, US patent 2406878

1947

Dupont introduces the pentaerythritol type alkyd paint, which is introduced two years later in UK [Standeven].

1948

First use of styrene-butadiene latexes in architectural paints – Glidden’s ‘Spred Satin®’.
Verwey and Overbeek publish their contribution to what became DLVO theory [E. J. W. Verwey and J. Th. G. Overbeek, Theory of Stability of Lyophobic Colloids, Elsevier, Amsterdam, 1948]

1947 – 1950

Epoxy resins commercialized [1].

1949

Kienle publishes on alkyd resins that dry much faster [R. H. Kienle, Ind. Eng. Chem. 41, p.726 (1949)].

1950

Hildebrand, in the third edition of his book coins the term ‘solubility parameter’ [Hildebrand, J. H., and Scott, R. L., “The Solubility of Nonelectrolytes,” Chap. XI (Reinhold Publ. Corp., New York, N.Y., 1950)]
M. Van der Waarden begins to understand steric stabilization of colloids in “Stabilization of carbon black dispersions in hydrocarbons”, Journal of Colloid Science, 5 317-25 (1950)
Unsaturated polyester resins appear [1], probably following Carothers’ work.
Natrosol® registered as trademark for alkali soluble cellulose ethers, and enters the market for thickeners.
Research into epoxy coatings at Devoe and Reynolds Inc.

1951 – 1955.

Epoxy-polyamide resin systems are introduced[1].

1951

Acrylic polymers for emulsion paints under development.
DuPont introduces the chloride process for refining TiO₂ at its Edgemoor plant.

1952

Powder coatings invented in Germany for fluidized bed use.
Thixotropic alkyds (in some ways the forerunner for hydrocarbon environments of associative thickeners for aqueous systems).

1953

First all-acrylic latex introduced commercially: Rhoplex® AC-33 in USA, (= Primal™ AC-33 in Europe).

1954

Thixotropic alkyd resins introduced [1].

1955

Water soluble/dispersible thermosetting resins introduced, e.g. alkyds and acrylics [1].

1956

G. L. Brown's research into latex film formation ["Formation of Films from Polymer Dispersions," J. Polym. Sci., Vol. 22, pp. 423 – 434 (1956).

Commercial production of isophthalic acid [Alkyd Resins by C. R. Martens, Reinhold Publishing Corporation NY 1961. (Chapman and Hall Ltd. London)].

Shell introduces amine and polyamide cured epoxy resins.

1956 – 1960

General Motors uses acrylics and acrylic-melamine resins in place of some of the cellulose nitrate and alkyd coatings for automotive finishes.

Urethane Oils and alkyds, thermoplastic acrylics for lacquers, thermosetting acrylics for enamels, silicone copolymers [1].

Crosslinking latexes are introduced [17].

1957

George Brewer develops anodic electrophoretic coatings at Ford Motor Company. See introduction in 1964.

1960

US patent 2930775, composition of a dispersing aid for pigments etc., maleic acid-diisobutylene copolymer ~ 1:1, corresponds to Tamol 731.

1961 – 1965

Fluoropolymers first introduced [look up Teflon].

1962

Texanol® registered as trademark by Eastman Chemicals and found use as a coalescing aid for latex paints by Eastman together with several customers and other resin suppliers [Del Rector, Eastman Chemical Company, private communication]. The discovery of the compound was somewhat accidental.

1960s- early 1970

First polyurethane dispersions (in water) were patented [D. Dieterich, "Aqueous Emulsions, Dispersions And Solutions Of Polyurethanes; Synthesis And Properties," Progress in Organic Coatings, 9 p. 281 – 340, (1981); Dr. R. Roesler, Bayer Chemicals, private Communication]

1964

Epoxy, acrylic and other resins used for anodic electrophoretic primers – pioneered by Ford Motor Company (Brewer, 1964). First electrophoretic (otherwise known as electrodeposition) paint tank filled at Ford Wixom works by PPG.

Eastman built the first plant producing Texanol as a commercial chemical. This coalescing additive made the application of latex paints possible over a much broader range of environmental conditions.[Del Rector, Eastman Chemical Company, private communication]

1966 – 1970

Ultraviolet and electron-beam cured polymer coatings appear for very fast cure requirements with low solvent emissions.

Non-aqueous dispersions of acrylics are developed.

1967

Los Angeles County invoked EPA Rule 66(5) that regulated the use of potentially harmful solvents in industrial coatings. This was to restrict photochemically (helped by UV) reactive solvents that combine with nitric oxide from automobiles and industrial processes to produce the well-known ‘smog’. Calculations quickly showed that ‘high solids’ coatings would be necessary. The world changed for coatings in the US. High Solids means ~ 60% solids by weight or higher.

UV wood coatings (Bayer) (see 1946).

1969

Commercialization of UV curing printing ink.

1970s

Start of serious work on thermoplastic and thermosetting polyester powder coatings and rapid development of UV curing compounds.

1970

Clean Air Act passed in US.

1971

Cathodic electrophoretic paints for automotive use introduced by PPG.

First non-mercurial mildewcide introduced: Skane M-8.

Acrylic polyelectrolyte thickeners introduced.

1973-75

Arab oil embargo, shortages of petrochemical feedstock puts more impetus behind chemistries that avoid use of lots of organic solvents and so attention turned to water-borne or high solids types.

1976

Cathodic electrocoat primer released by PPG.
Acrylic, polyester and urethane oligomers developed for high solids coatings.

1980s

The modern 'High Solids' age starts here. One might compare it to the Iron Age.

1981

Modified polyelectrolyte thickeners introduced, HASE (hydrophobically modified alkali-swellaible emulsions) and HEUR (hydrophobically modified urethane block copolymers).

1982

Epoxy water borne dispersions introduced.
Hard latex with hollow core introduced as opacifier.

1983

Group transfer polymerization [U.S. Patent, 4417034, November 22, 1983, DuPont Co.; S. N. Lewis., Letter to the Editor, Chem. Eng. News, 61, No. 48, 3 (1983)]. New method of tailoring very specific designs of polymers.

1983 – 86

Acceptance of powder coatings in several niche markets, based on polyesters combined with epoxies, triglycidyl isocyanurate etc.

1987

ISO 9000 is born from BS 5750. ISO 9000 is essentially a standard for organizations to create their own standards; requires strict adherence, follow-up and improvement.

Analytical Instrumentation

Methods such as IR, FTIR, UV, NMR, XRD, Raman, TGA, DTA, DSC, ESCA-XPS, Auger, SEM, TEM, DMTA (torsional braid analysis), Rheometers, MS, Chromatography, are all techniques that have made a major contribution to the science and technology of polymers and coatings. This section is very incomplete, and additions are welcome since it represents major enablers in the 2nd chemical revolution. A good starting reference to the history of instrumentation is "The History and Preservation of Chemical Instrumentation," Eds John T. Stock and Mary Virginia Orna, D. Reidel Publishing Co. (Springer), 2008

Mass Spec history is available at <http://masspec.scripps.edu/MSHistory/histpers.php> and see also S. Borman, H. Russell, G. Siuzdak, "Mass Spec Timeline" TODAY'S CHEMIST AT WORK, September, 47-49. (2003)

Crystallography and X-ray diffraction started with von Laue and Bragg in 1912 and a useful history can be found in J.-L. Hodeau, R. Guinebretiere, "Crystallography: past and present," Appl. Phys. A 89, 819 -823 (2007).

1881

Infrared absorption first studied in by Abney and Festing.

1903

Russian botanist Mikhail Semenovich Tswett, coined 'chromatography' from Latin for color writing, reports column adsorption chromatography. He passed extracts of plant tissue through a chalk column to separate pigments by differential adsorption. [M. S. Lesney, "Chromatography, A brief history of "color writing", Today's Chemist at Work, 1998, 7 (8), 67-68, 71-72].

1931

Richard Kuhn and others use chromatography to separate isomers of polyene pigments, showing that this was a more widely useful technique [M. S. Lesney, "Chromatography, A brief history of "color writing", Today's Chemist at Work, 1998, 7 (8), 67-68, 71-72].

1920-1930s

Further research done in universities on infrared spectroscopy.

1934

Don Brookfield sells the first dial viscometer.

1941

Beckman makes the first commercial infrared spectrometer.
Vitamin A is discovered to absorb in ultraviolet part of spectrum which is then used in US to check that military rations had vitamins.

1946

Purcell, Torrey, and Pound at Harvard (Purcell et al., 1946) and Bloch, Hansen, and Packard at Stanford (Bloch et al., 1946) independently found that they could detect characteristic magnetic moments of spinning atomic nuclei, i.e. nuclear magnetic resonance, NMR.

1953

First NMR spectrometer made by Varian Associates, HR-30.

Synthetic Pigments

N.B. At present, most of the entries for TiO₂ are above.

Egyptian Antiquity (4th Dynasty ~ 2500)

Egyptian blue, a glass really, (Cuprorivaite) CaO.CuO.4SiO₂

Cobalt used to colour materials, such as glass (and ground to make a pigment in medieval times, “smalt”), and pottery glazes – probably occurred around whole of Middle East.

Chinese Antiquity (~ 800 B.C.)

Chinese Blue and Purple, similar compositions to Egyptian blue but with barium instead of calcium.

Mayan Antiquity, 4th - 8th (?) Century A.D.

Maya Blue, indigo intercalated into palygorskite clay [G. Chiari et al.]. This is an example of what has become a very modern approach to nanocomposites!

1704 (approx)

Prussian blue introduced, i.e. Fe₄[Fe(CN)₆]₃.14 – 16 H₂O. First synthetic pigment of the modern(?) era.

1828 (approx)

Ultramarine blue.

1905

Red β-naphthol [“Industrial Organic Pigments,” W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley]

1907

Toluidine red (PR 3) [“Industrial Organic Pigments,” W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley]

1909

Hansa yellow (PY 1) first made in Germany – monoazo pigment that is usefully light stable [“Industrial Organic Pigments,” W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley]

1916

First type of titanium dioxide pigment made. Farup and Jebsen in Norway invent the sulphate process for industrial production.

1919

First production of TiO₂ pigment (anatase mixed with barium sulphate) Frederikstad by the Titan Company.

1920

First synthesis of diffraction effect pigments materials using HgCl_2 platelets (Note use of material from fish scales dates back to 17th. Century).

1923

Anatase pigments were introduced in France [Napier et al.], but rutile pigments did not appear until the early 1940s

1930 approx

Interference pigments made with other heavy metals, lead, arsenic and bismuth salts as platelets. Note that in 1959 Merck makes basic lead carbonate (white lead) as an interference (platelet shaped particles) pigment.

Fluorescent paints made from anthracene dyes in shellac, by Robert and Joseph Switzer of Berkeley, California [Pinchin and Tsang].

1932

ICI in England introduce alkyd paint, based on technology from DuPont in USA.

1935

Commercialization of diarylide yellows (patented in 1911)

Phthaloblue appeared, a synthetic, organic pigment that is very light stable.

1938

Phthalogreen is commercialised ["Industrial Organic Pigments," W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley].

1948

DuPont commercialise the chloride process for making rutile TiO_2 pigments.

1954

Disazo condensation pigments ["Industrial Organic Pigments," W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley]

1955

Quinacridones - intense, stable organic red pigments ["Industrial Organic Pigments," W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley]

1956

Perylene chemistry pigments, versatile chemistry that produces cheaper, but less stable red pigments than quinacridones.

1960

Benzimidazoline series of pigments appear ["Industrial Organic Pigments," W. Herbst, K. Hunger, 2nd. Ed. 1997, VCH-Wiley]

1963

DuPont patents metal oxide (TiO₂) coated mica flakes as interference effect pigments, closely followed by patents from Mearl in 1964.

1971

Use of aluminium flake pigments in metallic effect coatings for Lincolns. The flake pigments were made by Avery [G. P. Bierwagen, NDSU, private communication].

1972

Dupont, then others, supply titanium dioxide pigments in slurry form to the US paint industry.

1978

White lead pigments banned in US.

1984

Use of interference effect pigments in automotive use [VCH Interference Pigment book].

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