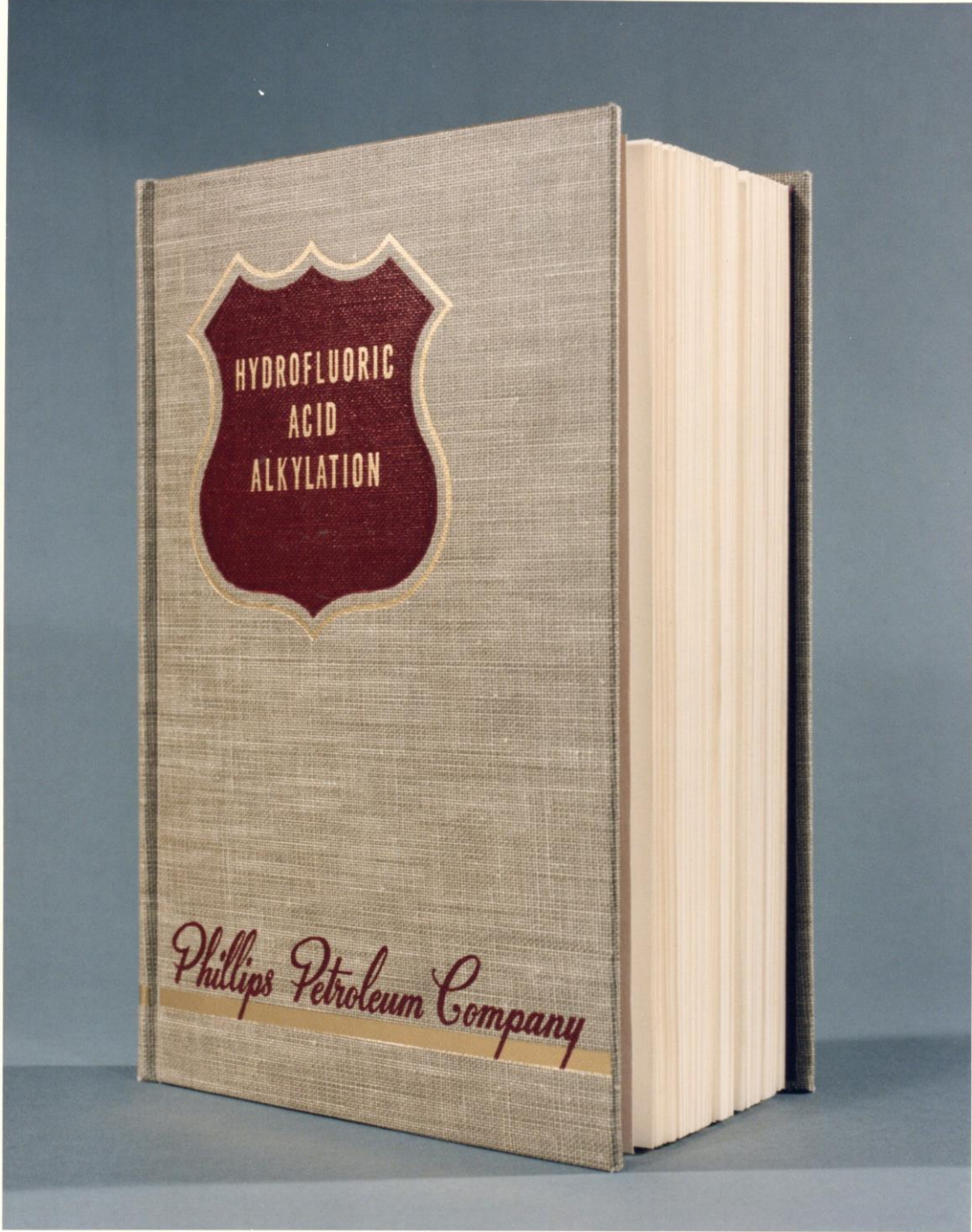


A Brief History of HF Alkylation-- 80+ Years of Events that have Resulted in Improved Safety and Reliability

Larry Shoemaker





Post WWII

- High octane aviation gasoline demand wanes
- 1950's-1980's Hi compression automobile engines require “premium” gasolines
- Leaded motor fuel phase out requires higher octane blending components; i.e. alkylate. In US, all on-road automobiles built after 1975 required unleaded. In 1996, US EPA banned sale for all motor vehicles and by 2021, a worldwide ban was achieved
- Ethanol blends into motor gasoline, requiring increased alkylate use for RVP control
- MTBE
- Alkylate remains a “best-blend stock” (low sulfur, hi RON/MON, no aromatics)

Significant Events

- 1984 Bophal India - MIC event
- 1986 AMOCO desert - HF release tests
- 1987 Marathon Texas City - HF settler release
- Incidents in Southern California - (SCAQMD)
- 1990 EPA's Hydrogen Fluoride Report to congress

Evolution of API RP-751

January 1990	API-RP-750, Management of Process Hazards
1990	EPA Report to congress on HF
February and April 1991	API background papers on the use of HF acid in the petroleum refining Industry
June 1992	1 st Edition, 33 pages
February 1999	2 nd Edition, 37 pages
June 2007	3 rd Edition, 45 pages
May 2013	4 th Edition, 67 pages
August 2021	5 th Edition, 174 pages

Safety and Reliability

Leak Detection Early Days

- Operator unit checks (see, smell, hear)
- Tell-tale hole drilling in piping systems
- Acid Detection paint
- HC detectors
- 18-24 Month T/A cycles typical-physical inspection, iron fluoride scale removal

Safety and Reliability

Leak Detection Current

- Operator unit inspections
- Color video cameras
- HC and HF detectors (point source, beams, etc)
- Acid detection paint
- UT testing and X-ray of piping and small-bore piping

Safety and Reliability

Mitigation Early Days

- Proper design-materials of construction
- Water cannons for fire protection

Safety and Reliability

Mitigation Current

- Spare parts MOC control (dedicated warehouse area for HF alky)
- Water cannons, sprays and water walls
- Remote operated block valves
- Settler internal baffles
- Rapid acid dump systems (RATS)
- Reduced volatility catalysts





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